RESEARCH ARTICLE

Homolytic Reactive Mass Spectrometry of Fullerenes: Interaction of C₆₀ and C₇₀ with Ketones in the Electron Impact Ion Source of a Mass Spectrometer and the Comparison of Results with Those of Photochemical Reactions of C₆₀ with Several Ketones in Solution

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Abstract

Our previous investigations showed that homolytic reactions of C₆₀ with a number of perfluoroorganic and organomercury(II) compounds occurring under electron impact (EI) in the ionization chamber (IC) of a mass spectrometer could predict the reactivity of C₆₀ towards these compounds in solution or solid state. To expand the scope of this statement, C₆₀ and C₇₀ have been reacted with ketones RCOR₁, where R and R₁ are alkyl, aryl, benzyl, and CF₃, in an IC under EI to yield products of the addition of R[•] and R₁[•] radicals to the fullerenes, paramagnetic ones being stabilized by hydrogen addition and loss. Experimental evidence in support of a mechanism involving homolytic dissociation of ketone molecules via superexcited states to afford these radicals that react with the fullerenes at the IC surface has been obtained. As anticipated, the reactions between C₆₀ and several ketones conducted in solution under UV irradiation have afforded Me-, Ph-, and CF₃-derivatives of C₆₀. However, some other products have been identified by mass spectrometry and their formation is reasonably explained. When decalin has been employed as a solvent, decalyl derivatives of the fullerene have been found among the products and the (9-decalyl)fullerenyl radical has been registered by EPR. Thus, incomplete but reasonable conformity of the results of the reactions of fullerenes with ketones in an IC under EI with those of the reactions of the same reagents in solution under UV irradiation has been demonstrated, and the former results can predict the latter ones to a reasonable extent.

Keywords: Fullerenes, Ketones, Reactive mass spectrometry, Electron impact, Photochemical reactions

For the preliminary report see reference [1]

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Introduction

Mass spectrometer is an instrument designed for work with ions. However, the ionization chamber (IC) of a mass spectrometer is a chemical reactor where bimolecular reactions not involving ions can occur, provided the

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corresponding reactants are introduced in the IC in sufficiently high amounts. Primarily, it relates to homolytic reactions since radicals are often formed under the energetic influence upon molecules in an IC, e.g., in the course of fragmentation of molecular ions obtained in the electron impact (EI) ion source, or in the plasma generated in the chemical ionization (CI) source of mass spectrometers. They can further react with molecules [2–7]. On the other hand, fullerenes are well known as good acceptors of radicals due to a plenty of double C=C bonds in their molecules [8]. In line with all this, McEwen and co-workers found that radical alkylation of C₆₀ took place under conditions of negative-CI with methane as a reagent gas [9]. In our earlier paper, we reported the radical trifluoromethylation of C₆₀ and C₇₀ by the reactions with the Scherer radical (C₉F₁₉•), a mixture of perfluorononenes (C₉F₁₈), and β-fluorosulphatotetrafluoroethylidheptafluoroisopropylmethyl radical (C₉F₁₈OSO₂F•) occurring in the IC of the EI source of a mass spectrometer [10]. In 2009, we published two papers evidencing that the radical trifluoromethylation, phenylation, and carboranylation of C₆₀ and C₇₀ proceeded in the IC when the fullerenes interacted with the corresponding organo- and organoelement mercurials [11, 12]. It is worth noting here that in spite of all difference in conditions (high energetic influence over the reactants, the absence of solvent, and so forth), given the evidence that a certain radical reaction proceeds in an IC, one can think about implementing the analogous reaction in solution. In other words, the homolytic reactive mass spectrometry of fullerenes (homolytic reactions of fullerenes with other species proceeding in an IC and their mass spectral monitoring) can serve as a tool for understanding what reactions of fullerenes one can try to carry out in solution (or in solid state/phase), and what energetic influence would be suitable here. In addition, it should be noted that the reactions in an IC as tests for the possibility to implement the analogous processes in a flask or chemical reactor have those advantages that they require micro amounts of reactants, occur rather quickly, and the products can be identified without delay.

Here we report the results of our investigations on the reactions of C₆₀ and C₇₀ with various ketones in an IC under EI and some photochemical ones between the same reagents in solution. The choice of ketones as reactants was favored by the fact that their molecular ions dissociate eliminating the corresponding organic radicals, thus providing the possibility for radical functionalization of fullerenes to occur by analogy with trifluoromethylation and so forth reported in references [10–12].

Experimental

C₆₀ (99.98%) was from a producer in Nizhnii (Novgorod, Russia). C₇₀ was prepared at the University of Sussex (Brighton, UK). They were used without any additional purification unless otherwise specified. Commercial grade preparation of acetone (**1**) was distilled in argon, while that of

acetone-d₆ (**1-d₆**) was not additionally purified. Commercial grade acetophenone (**2**) was also distilled in argon. Hexafluoroacetone (**3**) was bubbled through concentrated. H₂SO₄. Commercial grade benzophenone (**4**) was crystallized from ethanol (m.p. 44–46 °C). Phenylacetone (**5**) kindly given by Professor Belousov was distilled in vacuum. A distilled in vacuum sample of dibenzyl ketone (**6**) and distilled one of phenyl trifluoromethyl ketone (**7**) were kindly presented by Drs. Khodak and Gorunov, respectively. A sample of α-naphthyl phenyl ketone (**8**) was kindly given by Professor Ginsburg. Commercial grade methyl ethyl ketone (**9**), methyl butyl ketone (**10**), diethyl ketone (**11**), dibutyl ketone (**12**), and the solvents (decalin and benzene) were distilled in argon.

The mass spectrometry (MS) experiments and analyses of the reaction mixtures, the latter unless otherwise indicated, were carried out with a Kratos MS890 magnetic sector mass spectrometer (Manchester, UK) under EI of 70 eV and the temperature of the IC of 300 °C. A Carlo Erba Mega Series Gas Chromatograph (Carlo Erba Strumentazione, Milano, Italy) equipped with a 15 m methylsiloxane elastomer coated fused silica capillary column was attached to the spectrometer.

The procedures (*A* and *B*) employed to carry out the reactions in the IC were analogous to those reported earlier [10]. Generally, when the *A* method was used, fullerenes were inserted into the IC on the tip a quartz needle while ketones (1 μL) were introduced via the chromatograph. In the case of ketone **3** (gas), 1 mL of it was injected. If procedure *B* was used, a ketone was placed inside a capillary ampoule, fullerene applied onto the outer surface of the open end of the ampoule, and the ampoule end was introduced into the IC.

The monitoring of the reactions by electronic paramagnetic resonance (EPR) spectroscopy was performed with a Varian E-12A EPR spectrometer except as otherwise noted. The measurements of EPR characteristics of the (9-decalinyl)fullerenyl radical were made on a Bruker EMX-10/12 X-band (ν=9.3 GHz) digital EPR spectrometer.

The experimental protocols used to carry out the reactions of C₆₀ with ketones in solution under ultra violet (UV) irradiation are given in [Online Resource](#).

Results and Discussion

Reactions of C₆₀ and C₇₀ with Ketones in the IC of the EI Ion Source of a Mass Spectrometer

By application of methods *A* and *B* mentioned above, various ketones have been shown to react with C₆₀ in the IC under EI furnishing the positive molecular ions of methyl, aryl, benzyl, and trifluoromethyl derivatives of the fullerene. The reactions were accompanied by hydrogen addition to products and hydrogen loss from them (Scheme 1). Mass spectra obtained in the course of experiments with C₆₀ and acetone (**1**), and acetophenone (**2**) performed by procedures *B* and *A*, respectively, were given in the preliminary communication [1]; those obtained with the use of methods *A* and *B*, respectively, are presented in

		procedure →		A	B
1	R, R ₁ = Me	n + m =	1 - 7	1 - 16...	
2	R = Ph,	n = 0, m =	1 - 4	1, 2	
	R ₁ = Me	n = 1, m =	0 - 2	0, 1	
		n = 2, m =	0 - 2	0	
		n = 3, m =	0, 1		
3	R, R ₁ = CF ₃	n + m =	1 - 6		
4	R, R ₁ = Ph	n + m =		1 - 3	
5	R = Bn, ^a	n = 0, m =	1, 2		
	R ₁ = Me	n = 1, m =	0, 1		
6	R, R ₁ = Bn	n + m =		1	
7	R = Ph,	n = 0, m =	1, 2		
	R ₁ = CF ₃	n = 1, m =	0 ^b		
8	R = α-naphtyl	n = 0, m =		1	
	R ₁ = Ph	n = 1, m =		0	

^a Benzyl; ^b at 320 °C

Scheme 1. Products from the reactions of C₆₀ with ketones RCOR₁ performed in an IC under EI

Online Resource (Figure S1). Two other mass spectra illustrating the Scheme are depicted in Figures 1a and b. Mass spectra for the reactions with the rest of the compounds from Scheme 1 are given in Online Resource as Figures S2 and S3 (also see note S1 in Online Resource where the possible effect of fragment ions on the mass spectra discussed is shortly considered).

In our earlier paper [10] and preliminary communication on the reaction of C₆₀ with ketones [1], several arguments were given in favor of the fact that the reactions of C₆₀ with perfluoroorganic compounds and ketone 1 in an IC occurred due to thermally and/or EI initiated homolytic dissociation of the last-named reactants to give CF₃· and CH₃· radicals, respectively. These radicals were supposed to react with C₆₀ at the IC surface, with the products undergoing ionization after vaporization. Verification of such homolytic mechanism involving EI initiation for the reactions of fullerenes with ketones in an IC has been obtained in the present work by means of its detailed investigation in the case of the reaction between C₆₀ and 1. The description of the study is given further in the appropriate paragraph and the results are summarized in Scheme 2. In the context of this mechanism paramagnetic fullerene derivatives are initially formed due to

addition of radicals generated by ketones under EI to fullerenes. They should be prone to stabilization by the addition of the next radical or hydrogen addition and loss and undergo it as clearly seen from the monoisotopic (¹²C, ¹H) mass spectra for four groups of the products from the reaction with ketone 1 performed by both procedures, A and B, since the even mass ions prove to be the most abundant in each product cluster (Table 1). The spectra were derived from aggregated single magnetic scan spectra by application of the iteratively used program SCIPE [13], with the intensities of the first ion peaks from each group taken as the starting ones. They were averaged over several runs.

The mono- and poly-addition of methyl radicals accompanied by hydrogen addition and loss have also been observed for the reactions between C₆₀ and mixed ketones, methyl ethyl ketone (9) and methyl butyl ketone (10) (Figure S4 in Online Resource). The molecular masses of some methyl adducts of C₆₀ coincided with those of ethyl and butyl ones taking into account the processes of hydrogen addition and loss mentioned above. This made impossible immediate determination from the mass spectra whether the ethyl transfer from 9 and that of butyl from 10 occurred. Intending to overcome this difficulty, the reactions were carried out with symmetrical ketones, diethyl- (11) or dibutyl ketone (12). However, it turned out unexpectedly that peaks corresponding to the addition of methyl radicals to C₆₀ were present in the mass spectra (Figure S5 in Online Resource and Table 1). These peaks did not belong to fragment ions of ethyl or butyl derivatives of C₆₀. Actually, the molecular ions of butylhydrofullerenes C₆₀Bu_nH_n (n = 1–4), a mixture of which was prepared by successive treatment of C₆₀ with ⁿBuLi and aqueous CF₃COOH, do not fragment in such a manner. It is also valid for ethyl derivatives of C₆₀ obtained by the reaction of C₆₀ with 11 in solution. So, there are no doubts that additions of methyl radicals to C₆₀ occur in the reactions of the latter with 11 and 12 in an IC.

Hence, we encountered here with the same case that methyl additions could mask ethyl, and butyl ones. In this connection, it is essential to consider the results of the reactions of C₆₀ with ketones 5 and 6. These ketones have benzyl (Bn) radicals attached to the CO group, so that they are in principle capable of dissociation under EI, like ketones 9 and 11, via cleavage of as the OC–C bonds so the adjacent C–C ones to give Bn· and Ph· radicals, respectively. With that, the products of their addition to C₆₀ can be identified by MS without difficulties. In fact, Figures S2a and S2b in Online Resource show that as benzyl so phenyl additions to C₆₀ occurred in the reactions with these ketones, the latter providing HC₆₀Ph⁺ radical cation after stabilization of the adduct and EI (its peaks in the mass spectra are not due to the fragment ion of the benzyl derivatives since fragmentation of this kind was not observed in the spectra of benzyl derivatives prepared in solution by another reaction ([14] and unpublished results thereof). Each radical attached to the carbonyl group in all other species from Scheme 1 was transferred to C₆₀ in the course of the reactions between

Figure 1. Mass spectra in the high mass region recorded in the course of runs conducted in an IC at the electron energy of 70 eV and the IC temperature of 300 °C: (a) by method A with C₆₀ and hexafluoroacetone (**3**); (b) by method B with C₆₀ and α-naphthyl phenyl ketone (**8**); (c) by method A with C₇₀ and acetone (**1**); (d) by method A with C₇₀ and acetophenone (**2**). The ion peaks due to C₇₀ derivatives bearing two phenyl groups are more pronounced in the spectra from other magnetic scans (see the inset)

them. These facts allowed us to suggest that the ethyl radical transfer to the fullerene from ketones **9** and **11** and that of ethyl and butyl ones from **10** and **12** had to take place. The following points support this statement.

1. In the monoisotopic spectra (method A), the ratio of the 748 Da ion peak intensity to that of 750 Da is 0.99 ± 0.18 (standard deviation (SD)) in the case of **11** versus 0.60 ± 0.13 for the reaction with ketone **1**. Both monoisotopic spectra (Table 1, the first group) show the methyl adduct to undergo stabilization via the loss of a hydrogen atom to a greater extent than via its addition. This is highly probable to be valid for the ethyl adduct, and a contribution of it to the second product group, if it exists, ought to increase the ratio as compared with that for **1**. Thus, the contribution of this adduct stabilized by hydrogen addition and loss appears to be responsible for the found increase in relative intensity of the 748 Da ion peak in the case of the reaction with **11**.

Additional arguments based on the comparison of the integrated intensities of the first two ion clusters of the

products derived from aggregated one-scan mass spectra for the reactions of C₆₀ with ketones **1**, **11**, and **12**, and indicating that at least one ethyl radical adds to the fullerene in two last-named reactions are given in [Online Resource](#).

2. For the products from the reaction of C₆₀ with ketone **12** performed by method A, the ratio of the intensity of the 778 Da ion peak to that of the 780 Da ion in the monoisotopic mass spectrum is 3.1 ± 0.1 . In the case of ketone **1**, the ratio is an order of magnitude less (0.3 ± 0.06). The comparison of these values shows the monoaddition of butyl radical to occur in the reaction of C₆₀ with **12**. This affords radical [•]C₆₀Bu stabilized further by hydrogen addition and loss to give (after EI) the 778 and 776 Da ions, respectively, while the product of quadruple addition of methyl radicals provides the 780 Da ion, C₆₀(CH₃)₄⁺⁺ dominating in the fourth product cluster in the case of ketone **1** (Table 1).

For the reaction of C₆₀ with perfluoroorganics also accompanied by hydrogen addition, the main source of hydrogen atoms proved to be hydrogen-containing com-

Table 1. Abundances (I_{rel}) of Monoisotopic (^{12}C , ^1H) Ions Normalized to 100% Total of Each Group for the First Four Groups of the Products from the Reactions of C_{60} with Ketones Me_2CO (**1**), Et_2CO (**11**), and Bu_2CO (**12**) in the IC Under EI

<i>m/z</i>	Ion [...]⁺	Ketone				
		1	11		12	
		Method				
		<i>A</i>	<i>B</i>	<i>A</i>	<i>A</i>	<i>B</i>
<i>I_{rel}</i> (%)						
The first group of the products						
734	C ₆₀ CH ₂	63	30	49	37	20
735	C ₆₀ CH ₃	4	4	8	8	4
736	HC ₆₀ CH ₃	31	37	32	44	50
737	H ₂ C ₆₀ CH ₃	0	6	1	6	4
738	H ₃ C ₆₀ CH ₃	1	13	6	2	12
739	H ₄ C ₆₀ CH ₃	1	5	2	1	5
740	H ₅ C ₆₀ CH ₃	0	5	2	2	5
The second group of the products						
748	C ₆₀ C ₂ H ₄	31	14	44	31	21
749	C ₆₀ C ₂ H ₅	1	4	1	12	4
750	C ₆₀ C ₂ H ₆	53	22	45	36	45
751	C ₆₀ C ₂ H ₇	1	9	1	6	6
752	C ₆₀ C ₂ H ₈	12	26	5	11	15
753	C ₆₀ C ₂ H ₉	1	11	3	2	3
754	C ₆₀ C ₂ H ₁₀	1	14	1	2	6
The third group of the products						
760	C ₆₀ C ₃ H ₄	16	10	25	14	12
761	C ₆₀ C ₃ H ₅	1	1	2	2	2
762	C ₆₀ C ₃ H ₆	20	9	23	17	17
763	C ₆₀ C ₃ H ₇	3	3	3	9	8
764	C ₆₀ C ₃ H ₈	20	9	14	24	22
765	C ₆₀ C ₃ H ₉	8	9	2	5	2
766	C ₆₀ C ₃ H ₁₀	18	17	10	15	15
767	C ₆₀ C ₃ H ₁₁	2	11	2	6	4
768	C ₆₀ C ₃ H ₁₂	8	15	8	4	13
769	C ₆₀ C ₃ H ₁₃	3	11	8	2	1
770	C ₆₀ C ₃ H ₁₄	1	12	3	2	4
The fourth group of the products						
774	C ₆₀ C ₄ H ₆	16	12	26	10	7
775	C ₆₀ C ₄ H ₇	1	2	1	1	3
776	C ₆₀ C ₄ H ₈	16	6	22	32	15
777	C ₆₀ C ₄ H ₉	1	2	5	4	1
778	C ₆₀ C ₄ H ₁₀	10	5	7	29	37
779	C ₆₀ C ₄ H ₁₁	2	5	7	4	0
780	C ₆₀ C ₄ H ₁₂	33	13	8	9	19
781	C ₆₀ C ₄ H ₁₃	5	10	4	3	1
782	C ₆₀ C ₄ H ₁₄	4	15	7	0	8
783	C ₆₀ C ₄ H ₁₅	5	9	2	4	1
784	C ₆₀ C ₄ H ₁₆	0	7	1	0	5
785	C ₆₀ C ₄ H ₁₇	3	8	5	1	0
786	C ₆₀ C ₄ H ₁₈	4	6	5	3	3

pounds adsorbed on the walls of an IC [10]. Since all ketones used but **3** contained hydrogen atoms, a question to be considered is whether they themselves also served as hydrogen providers. To elucidate this, C_{60} was reacted with hexadeuteroacetone (**1-d₆**). Mass spectra obtained were treated analogously to those for the reaction of C_{60} with **1** to give the monoisotopic in respect of carbon (^{12}C) spectra showing the distribution of ion abundances in the first two groups of the products from the reaction (Table S2 in Online Resource; cf. with values for the reaction with **1** in Table 1).

The 740 Da ion, $[\text{C}_{60}(\text{CD}_3)\text{D}]^{+*}$, with pronounced abundance is present in the first group of the reaction products. The second group (method *B*) displays the 760 Da ion containing two deuterium atoms added. All this indicates that in the reaction of C_{60} with ketone **1**, the latter itself should be involved as a hydrogen donor. However, protium atoms are also present in the products of the reaction between C_{60} with **1-d₆** (for example, in the 739 Da ion, and for method *B* in the 755, and 759 Da ones). The hydrogen incorporation takes place in the course of the reaction of C_{60} with perfluoroketone **3** as well. The most probable hydrogen (protium) source in both cases seems to be hydrogen-containing compounds adsorbed on the metal walls of the IC. Thus, these results show that both these compounds and ketones themselves, those that contained hydrogen atoms amenable to homolytic abstraction at 300 °C (all used except **3** and, probably, **4**, **7**, and **8**) served as the hydrogen sources in the discussed reactions.

C_{70} reacts with ketones **1**, **2**, **3**, and **11** analogously to C_{60} attaching from 1 to 3 Me, 1 Me, and 1, 2 Ph, between 1 and 3 CF_3 , and at least from 1 to 3 Me (highly probable, 1 Et), respectively. The reactions are also accompanied by hydrogen addition and loss except the latter in the case of ketone **3**. Figure 1 depicts mass spectra recorded during experiments with C_{70} and ketones **1**, and **2** (c and d, respectively). Figure S6 in Online Resource displays those for runs with **3** and **11**.

Mechanistic Studies of the Reaction Between C_{60} and Acetone (**1**) in an IC

The mass spectral data acquisition and treatment software used produces mass chromatograms (dependences of intensities of ion peaks or their groups with scan or time). For method *A*, they display an interesting feature: the C_{60}^{+*} curve drops significantly when the peak of **1** appears and this peak having decreased, increases together with the peaks of the products (Figure 2a). This can be caused by several effects connected with the pressure increase due to ketone **1** appearing in the IC. Thus, the maxima of the product traces are shifted in time relative to that of the m/z 58 (M^+ of **1**) ion peak curve. This suggests that the IC surface is involved as a reaction site.

Such characteristics of the curves enabled us to reveal whether EI was necessary for the reaction to proceed and to estimate the relative amounts of the products vaporizing from the IC surface. To do so, the reaction was carried with the filament switched off until the point where the bulk of ketone **1** was pumped out of the IC. The filament was then turned on, and the product peaks were registered (Figure 2b). This experiment was followed by another one with the filament turned on in the course of the entire run (Figure 2a). The mass spectra recorded after the time point when the filament was turned on were aggregated (34 magnetic scans) for each run and the integrated intensities of the peaks for first four groups of the products (they constituted the bulk of

Figure 2. Mass chromatograms recorded in runs with C₆₀ and acetone (**1**) carried out in an IC at 70 eV and 300 °C by: (a) standard method *A* and (b) method *A* with “the filament switched off”. The character of the curves for the other C₆₀ derivatives registered is similar; (c) peak intensities of ions related to those at the 30 V repeller potential versus the repeller potential: (A) of products from the reaction between C₆₀ and acetone (**1**) performed by method *A*. (B) of the *m/z* 101 ion formed due to the ion/molecule reaction of **1** with the acetyl cation

the products) determined. The averaged ratio of the first value to the second was $7.9\% \pm 1.6\%$ (SD). It means that at least 90% of the products were formed due to EI activation of one or both reagents. Most probably, the remaining ca. 10% resulted from the EI initiated reaction with the residual amounts of **1** rather than from a thermal reaction, or the respective peaks were background ones due to the ‘memory effect’ of the instrument.

Estimation of the relative amounts of the products vaporizing from the IC surface was performed by the comparison of the integrated intensities of product ions from the first four groups registered in standard method *A* runs from the time point where the filament was turned on in the conjugated “filament-switched-off” experiments with those of all such ions registered in the course of the runs (for the details see the description of analogous experiments on pages 277 and 278 of reference [10]). This gave a value of $65\% \pm 10\%$ indicating that the great amounts of the products actually vaporized from the IC surface to be registered after EI (see note S2 on this value and the description of experiments and their results indicating that the reaction did not proceed on the tip of a needle by which the fullerene was introduced into the IC in [Online Resource](#)).

The aforesaid characteristic of the mass spectra also suggested performing the following experiments that would indicate whether cations were involved in the process. The reactions were conducted with the decreased potentials of the ion-repelling electrode (repeller) with respect to the IC cage (RP) and the accelerating voltage (AV) switched off until the point where the peaks of the products had to appear. The latter was done since the electrostatic field could penetrate inside the

IC creating an additional cation-extracting effect. The integrated intensities of the first two groups of the product peaks were calculated from the spectra obtained by peak-summarizing over the scans registered after the time point when the RP was set to the standard 30 V and the AV turned on. These values were related to the analogous ones obtained for the conjugated runs with the RP of 30 V and the AV switched on in the course of the entire experiments, with peak aggregation commencing from the same time point as in the above-mentioned runs. Curve (A) of Figure 2c presents the averaged ratios obtained for the above experimental pairs versus the RP. The first two points demonstrate that the AV switching-out does not affect the results. At the same time, the curve slightly drops with the decrease in the RP. When the potential achieves the zero point, the ratio (averaged over six experimental pairs) turns out to be $75\% \pm 9\%$ (SD). It is essential to compare this curve drop with the results obtained from the analysis of mass spectra of ketone **1** recorded at the same values of the RP. If the input of **1** into the IC was sufficiently high, an ion/molecule reaction occurred between its molecule and the acetyl cation formed due to fragmentation of the molecular ion of **1**. This produced the *m/z* 101 ion. Curve (B) of Figure 2c shows the behavior of its intensity obtained by peak-summarizing over scans, normalized to that at the 30 V RP, and averaged over two runs, when the RP decreases. More than a 7-fold increase of the intensity is observed when RP falls to zero.

If cations were intermediates in the reaction of C₆₀ with **1**, the yield of the products would have been anticipated to increase with the decrease of the RP, since the cations would have been ejected less from an IC, and thus their partial pressure in the IC would have increased. Thus, the

comparison of curves (A) and (B) indicates that the secondary positive ions, namely, those formed due to fragmentation of the molecular ones of **1** were not involved in the reaction of C_{60} with **1** in the IC. Moreover, since the product ions were registered at the RP of initial 30 V so that there was no decrease in the sensitivity of the instrument, this relates in full measure to the molecular ions of C_{60} and ketone **1** themselves, and the neutral fragments of 1^{++} (for example, the radicals) could not contribute pronouncedly to the reaction as well. Since the negative ions could hardly be involved in the process under the applied conditions, the reaction appears to occur via a homolytic mechanism presented in Scheme 2 (see note S3 in Online Resource).

According to Scheme 2, the reaction begins with activation of acetone (**1**) molecules to a superexcited state (the state with the electronic excitation energy higher than the first ionization energy of the molecule) [15]. The activated molecules further homolytically decompose to furnish methyl radicals. The radicals are “hot” and should be deactivated in order to be capable of the reactions with C_{60} . The most favorable mode of this is the collision with the surface of the IC. The deactivated methyl radicals react with the fullerene adsorbed at the surface to furnish methylated derivatives of the latter. Paramagnetic species obtained are stabilized by addition of the next radical or by hydrogen loss and addition. The source of the hydrogen atoms appears to be both ketone **1** and hydrogen-containing compounds adsorbed on the IC surface. The products vaporize from the surface to be registered after EI.

All this agrees well with the findings of C. N. McEwen et al. which show mono- and multiple additions of alkyl radicals to C_{60} to occur at the IC walls under CH_4 -mediated negative-CI [9].

The reaction routes for the other ketones examined are apparently similar. For ketones **5**, **6**, **9**, **10**, **11**, and **12**, the homolytic dissociation of the species in superexcited states provides not only those radicals that have been attached to the carbonyl groups, but fragment ones, phenyls, methyls, and ethyls (probably, propyls for **10** and **12** as well), which add analogously to the fullerene core.

It is worth noting here that D. K. Bohme’s group published a great number of papers on the ion/molecule

reactions of C_{60}^{+} , C_{60}^{2+} , and C_{60}^{3+} isolated by the “selected-ion flow tube” technique with a large variety of species [16]. The authors of one of them (S. Petrie et al.) showed that C_{60}^{+} did not react with ketones **1**, **9**, **11**, and some others in helium at 294 ± 2 K and a pressure of 0.35 ± 0.1 torr, while C_{60}^{2+} reacted to furnish adducts like $(C_{60} \cdot (CH_3)_2CO)^{2+}$ [17, 18]. Conversely, when positive ions were generated from **1** under conditions of its self-CI (at $200^\circ C$ and *ca.* 10 Pa in an IC) and reacted with neutral C_{60} , C_{70} , and endometallofullerenes, acetylfullerenyl cations were formed [19–21]. Thus, the reaction products for these two ion/molecule modes were different from those obtained in the present work. This is apparently due to the fact that the reaction mechanisms differ, namely, it is a homolytic one in the last case.

Reactions of C_{60} with Ketones in Solution

Given validness of the radical mechanism mentioned, the simplest substitute for the electron beam in order to implement the analogous processes in solution seemed to be photoirradiation in the UV region of 200–400 nm. It is especially so, since ketones are known to undergo the Norrish type I cleavage (at C–CO bonds) providing radicals under such irradiation. However, these reactions are usually carried out in the gas phase if the radicals formed are not stabilized by an appropriate substituent (e.g., as in the case of ketone **6**). One of the main reasons of it is the recombination of the radicals in the solvent cage to give the starting ketone [22]. It can be supposed that if a ketone itself serves as a solvent the reaction with C_{60} could proceed. In fact, when a mixture of C_{60} and a large excess of ketone **2** was UV irradiated under stirring for 11.5 h, products of the addition of methyl and phenyl radicals to C_{60} , with paramagnetic those stabilized by hydrogen addition or loss, were detected by MS (Figure S7a in Online Resource). When mass spectra were summarized over scans, fullerene derivatives obtained due to the addition between one and not less than three methyl groups and one containing both a phenyl and a methyl group (peaks around that at m/z 812) were clearly revealed; of interest, also turned out groups of ion peaks at m/z 822, 824, 836, 838, 840, and 850–856 (Figure 3a). Their presence could be explained by the formation of the products of consecutive addition of methyl radicals to the phenylated derivative of C_{60} followed by hydrogen atoms and molecules loss (the latter, probably, under EI). However, the 824 Da ion is the most abundant in its group and the 838 Da is the second in abundance in the cluster. This may indicate that other processes are also involved. A plausible origin of all these ions is given in Scheme 3.

The pathways of Scheme 3 find support in several experimental findings: (1) when an analogous mixture of C_{60} and ketone **1** was UV irradiated under stirring for 5.5 h, a peak at m/z 776 was registered in the mass spectra along with those at m/z 734 and 736. The first one can be

Scheme 2. Homolytic mechanism suggested for the EI initiated reaction of C_{60} with acetone (**1**) in an IC

Figure 3. Mass spectra in the high mass region of the reaction mixture of C_{60} with: (a) acetophenone (**2**) after 11.5 h UV irradiation. The spectrum was obtained by peak-summarizing over 51 magnetic scans followed by averaging over two analyses (the background peaks were omitted), (b) acetone (**1**) after 5.5 h UV irradiation, (c) acetone (**1**) in decalin solution after 7 h UV irradiation, and (d) hexadeuteroacetone (**1-d₆**) in decalin solution after 7 h UV irradiation

attributed to the $C_{60}CHCOCH_3^{++}$ ion of the structure analogous to that of the 838 Da ion in the case of ketone **2**, while the last two obviously appear due to addition of a methyl radical to the fullerene core followed by hydrogen addition and loss. The low intensity m/z 792 ion (the analog of the 854 Da ion in the case of ketone **2**) appears to be due to the product of the addition of both the $\cdot CH_2COCH_3$ and $\cdot CH_3$ radicals to C_{60} (Figure 3b). The cyclization of the m/z 776 ion to give the m/z 774 one does not virtually occur since a hindered three-membered ring should be formed contrary to the case of ketone **2** where the analogous process leading to the 836 Da ion is probably promoted by the formation of a four-membered ring. These findings verify the part of Scheme 3 beginning from the addition of radical $\cdot CH_2COPh$ to C_{60} . (2) When the photoreaction of C_{60} with ketone **1** was performed in decalin (decalin was chosen as a

solvent since it dissolves C_{60} pronouncedly greater than hexane and insignificantly absorb light in the 300 nm region where ketones do), the molecular ion peaks of the products of decaliny radical addition to the fullerene followed by hydrogen addition and loss appeared in mass spectra along with the analogous ones of methyl radical addition (Figure 3c). The later was rather unexpected since contradicted the above statement that the Norrish type I cleavage of ketones is usually ineffective in solvents. The EPR monitoring of the process showed a signal from paramagnetic derivatives of C_{60} . At the same time, in the control experiment when the analogous decalin solution of C_{60} containing none of acetone was irradiated, small signals were registered in the EPR spectra and the MS analyses displayed only negligible amounts of decaliny derivatives of C_{60} . These results indicate that decaliny derivatives in the

Scheme 3. Ways of the formation of a number of MS-detected products from the photoreaction between C_{60} and acetophenone (**2**)

reaction with **1** were obviously formed via hydrogen atom abstraction from decalin by exited **1** and thus, exited **2** could abstract a hydrogen atom from ketone **2** that served as a solvent as well to give $\text{CH}_3\dot{\text{C}}(\text{OH})\text{Ph}^*$ radical involved in a route of Scheme 3. The further support to this route comes from the presence of the dominant peak at m/z 762 in the spectrum from the reaction of C_{60} with **1** in decalin (Figure 3c).

A priori, three following structures can be assigned to the corresponding product: $\text{C}_{60}(\text{CH}_2)_3$ formed due to addition of three methyl radicals to C_{60} , with each addition being followed by a hydrogen atom loss, $\text{C}_{60}\text{COCH}_2$ formed owing to the addition of CH_3CO^* followed by cyclization with the loss of a hydrogen atom, and $\text{HC}_{60}\text{C}(\text{OH})(\text{CH}_3)_2$ (molecular weight 780 Da). Its molecular ion should most probably decompose with the loss of water to furnish the $\text{C}_{60}\text{C}(\text{CH}_3)_2^{++}$ radical cation (m/z 762) registered in the spectra. To make a choice between these structures, the

reaction was performed with ketone **1-d₆**. The broadened singlet from paramagnetic derivatives of C_{60} ($g=2.0026$) was registered in the EPR spectra, and the mass spectra showed the peak at m/z 762 to be shifted to the m/z 768 position (Figure 3d) thus excluding the second, oxygen containing, structure.

The first structure also seems highly improbable due to two reasons: (1) the treatment of the summarized over 90 magnetic scans spectrum for the reaction with **1** by the iteratively used program "SCIPE" produced the following values for the ion cluster under consideration (m/z , relative intensity in the cluster in percent): 759, 1; 760, 4; 761, 1; 762, 82; 763, 0; 764, 7; 765, 1; 766, 2; 767, 1; 768, 1. If this ion cluster arises due to the product of triple methyl radical addition to C_{60} , that means the loss of a hydrogen atom after each methyl addition proceeds almost exclusively to give the predominant 762 Da ion in the spectrum. This contradicts the finding that for the first group ions the ratio of the

intensity of $\text{HC}_{60}\text{CH}_3^{++}$ ion to that of $\text{C}_{60}\text{CH}_2^{++}$ is equal to 1.2, i.e., the hydrogen addition occurs pronouncedly. Results of the reaction of C_{60} with ketone **11** in decalin under UV irradiation also argue against the above hypothesis. The reaction was monitored by EPR and MS. A relatively intensive broadened signal from alkylfullerenyl radicals was observed in the EPR spectrum taken after 7 h irradiation, and the mass spectra showed ion peaks of the products formed due to the addition of up to 5 ethyl radicals to the fullerene, all groups, including one of the triple addition, containing products with acquired hydrogen atoms (Figure 4a). Moreover, e.g., one of the two most abundant ions in the third ion cluster of the monoisotopic spectrum turned out to be the 810 Da ion ($\text{H}_4\text{C}_{60}\text{Et}_4^{++}$). Note, the Figure 4a spectrum also contains ions due to the products of the decalyl radical addition to C_{60} and mixed ones of the decalyl and ethyl radicals additions. (2) The integrated intensity of the peaks of the first ion cluster for the fullerene derivatives from the 7 h reaction of C_{60} with ketone **1** in decalin relates to the second, and the third ones in the

spectrum obtained by peak-summarizing over scans as 1:0.29:2.2. It appears to be unreasonable, especially with such a gap for the double addition products, whether to accept the route of the subsequent addition of methyl radicals to C_{60} involving the predominant hydrogen atoms loss for the formation the triple addition products. Here we can again appeal to Figure 4a, where we see a reasonable decrease in intensities of the respective ion clusters with the increase of the amount of ethyl radicals added (the same is valid for the summarized over scans mass spectrum).

Thus, the most probable structure of the 762 Da ion is $\text{C}_{60}\text{C}(\text{CH}_3)_2^{++}$, and this attests a route leading to the 824 Da ion in Scheme 3. The scheme shows, however, another route producing the m/z 824 ion of a different structure. Support for this route is provided by the analogy with the photo-reaction of C_{60} with benzaldehyde in decalin. The rather intensive 824 Da ion was present in mass spectra of the reaction mixture, and the respective product had to be formed via the addition of $\text{PhCO}^{\bullet}$ to C_{60} like that depicted in Scheme 3. No alternative exists in this case.

Figure 4. (a) Mass spectrum in the high mass region of the sample taken from the reaction mixture of C_{60} and diethyl ketone (**11**) in decalin after 7 h UV irradiation; (b) (A) EPR spectrum of $\text{C}_{60}(9\text{-decalyl})$ radical obtained in the course of UV irradiation of C_{60} and small amounts of acetone (**1**) in decalin solution at 295 K and (B) simulated EPR spectrum of the radical; (c) (A) EPR spectrum of the reaction mixture of C_{60} and acetone (**1**) recorded after 20 min irradiation by the focused light of a 1000 W ARC lamp power supply, model 69920 at 295 K and (B) LDI-TOF mass spectrum in the high mass region of the sample of the reaction mixture taken after 20 min irradiation; (d) mass spectrum in the high mass region of the reaction mixture of C_{60} and phenyl trifluoromethyl ketone (**7**) in decalin after 1 h UV irradiation

To get more detailed information on a decalinyllfullerenyl radical forming in the reactions in decalin, the reaction of C_{60} with ketone **1** was performed in the cavity of a Bruker EMX-10/12 X-band EPR spectrometer with decalin solution of C_{60} and small amounts of ketone **1**. The reaction mixture was irradiated with the unfiltered light of a high-pressure mercury lamp (1 kW). A multiplet from a decalinyllfullerenyl radical with $g=2.0024$ and hyperfine splitting constants $a(1H)=0.095$ G, $a(4H)=0.151$ G, and $a(4H)=0.010$ G (poor resolution) was registered (Figure 4b, spectrum A). The spectrum is consistent with the simulated one for the (9-decalinyll)fullerenyl radical (Figure 4b, spectrum B).

The reaction of C_{60} with ketone **1** without additional solvent was performed under the unfocused light of a relatively weak intensity from a 375 W medium-pressure mercury lamp. As a result it went to a small extent as seen from the rather low peak intensities of the products and the fact that only one methyl radical effectively added to C_{60} (Figure 3b). The latter allowed, however, clear detection of such product as $C_{60}CHCOCH_3$ (776 Da). To get the more effective addition of methyl radicals to the fullerene, the reaction has been conducted in the cavity of the Bruker spectrometer under the focused light of a more powerful lamp (1 kW). Actually, a signal from paramagnetic derivatives of C_{60} has been registered in the EPR spectrum, and the laser desorption/ionization time-of-flight (LDI-TOF) mass spectrum taken after 20 min irradiation displayed peaks due to mono- and multiple additions of methyl radicals to the fullerene (Figure 4c, spectra A and B, respectively). The peak intensities of the forth ion cluster in the mass spectrum increase beginning from the 776 Da ion due to the contribution from the $C_{60}CHCOCH_3^{+}$ radical cation. Moreover, ions due to products of methyl radical additions to the above (neutral) product can contribute to the next ensuing ion clusters.

Two other compounds from Scheme 1 tested for the reactivity towards C_{60} in decalin solution under UV irradiation are PhCOMe (**2**) and PhCOCF₃ (**7**). In the first case mass spectra displayed products of addition of methyl, phenyl, and decalinyll radicals followed by hydrogen addition or loss (Figure S7b) in Online Resource). The reaction of the latter with C_{60} afforded the products of addition of a CF₃ group and a Ph group followed by the addition of hydrogen atoms. Figure 4d presents a mass spectrum recorded after 1 h irradiation. As for the reactions in decalin with ketones **1**, **1-d₆**, **2**, and **11**, the spectrum also displays ions at m/z 856 and 858 corresponding to the products of decalinyll radical addition with the subsequent hydrogen addition and loss. However one cannot exclude a contribution from $(CF_3)_2C_{60}^{+}$ to the intensity of the latter.

Earlier, Krusic et al. reported the formation of benzyl fullerene adducts with a number of benzyls up to 15 via the reaction of C_{60} with benzyl radicals photochemically generated from ketone **6**. They also found peaks in the mass spectrum corresponding to mixed adducts with benzyl groups and one benzylcarbonyl group [23]. In a following work, Morton et al. registered the EPR signal from $(CH_3)_3C_{60}^{\bullet}$ obtained under UV irradiation of a solution of C_{60} and ketone **1**

in *tert*-butylbenzene [24]. These results provide valuable addition to the material of our article.

Conclusions

Thus, all ketones RCOR₁ examined react with C_{60} in the ionization chamber (IC) of a mass spectrometer under EI to furnish products of mono- and multiple additions of the corresponding radicals R[•] and R₁[•] to the fullerene core. The reactions are accompanied by hydrogen addition to paramagnetic products and the loss of a hydrogen atom from them, the latter in those cases where derivatives obtained contain hydrogen atoms liable to this. The sources of the hydrogen atoms prove to be both hydrogen containing compounds adsorbed at the metal walls of the IC and ketones themselves. C_{70} enters into the similar reactions with several such ketones. The experimentally supported homolytic mechanism is proposed for the reactions. It involves two main characteristics: the intermediate radicals are formed due to dissociation of ketone molecules being in superexcited states and these radicals react with the fullerenes at the IC surface. The former imparts an interesting feature to the reactions—if R and/or R₁ are Et, Bu, and CH₂Ph, besides these radicals, fragment radicals Me[•], Me[•], and Et[•], and Ph[•] are formed and add to the fullerenes, respectively. The above mass spectral studies have been undertaken by us not only as ends in themselves, but one of the major tasks of the present work has been to show that analogous reactions between fullerenes and ketones can proceed in solution, and they do react. Under quartz region UV irradiation as the simplest substitute of the irradiation by electrons, C_{60} interacts with such ketones as acetone (**1**), acetophenone (**2**), phenyl trifluoromethyl ketone (**7**), and diethyl ketone (**11**) with the transfer of the corresponding radicals R[•] and R₁[•] from the ketones to the fullerene. Thus, the concurrence of the results of the homolytic reactive mass spectrometry of fullerenes with those of the reactions between the same reagents in solutions is observed, certainly, to a reasonable extent. For example, apart from the reactions in the IC, some other products have been found in the UV irradiated reaction mixtures of C_{60} with ketones **1** and **2**, and their formation is reasonably explained. Besides, in all reactions in decalin as a solvent, products of decalinyll radical additions stabilized by hydrogen addition and loss have been identified. A special EPR study and the analysis of the spectrum involving the simulation procedure have shown that a radical forming in the course of the reaction with compound **1** in decalin is the (9-decalinyll)fullerenyl one. In general, the results obtained along with those already reported for the reactions of fullerenes with some perfluoroorganics and organo- and organoelement mercurials provide evidence that the homolytic reactive mass spectrometry of fullerenes can really serve as a quick tool for elucidation what fullerene reaction can be implemented in solution or in the solid state/phase and what modes would better be used for achievement of this purpose.

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References

- Shilova, E.A., Lyakhovetsky, Y.I., Tumanskii, B.L., Belokon', A.I., Nekrasov, Y.S.: Alkylation and Phenylation of [60]- and [70]-Fullerenes by the Reaction with Ketones in the Ionization Chamber of a Mass Spectrometer. *Mendeleev. Commun.* 176–177 (1999).
- McEwen, C.N., Rudat, M.A.: Fast Radical Reactions in a Mass Spectrometer Ion Source: Radical Addition to 7,7,8,8-Tetracyanoquinodimethane. *J. Am. Chem. Soc.* **101**, 6470–6472 (1979)
- McEwen, C.N., Rudat, M.A.: Radical Trapping in a Mass Spectrometer Ion Source. 1. *J. Am. Chem. Soc.* **103**, 4343–4349 (1981)
- Rudat, M.A., McEwen, C.N.: Gas-Phase Radical Structures. Radical Trapping. 2. *J. Am. Chem. Soc.* **103**, 4349–4354 (1981)
- McEwen, C.N., Rudat, M.A.: Isomerization of Gas-Phase Hydrocarbon Ions. Radical Trapping. 3. *J. Am. Chem. Soc.* **103**, 4355–4359 (1981)
- Stöckl, D., Budzikiewicz, H.: Negative-Ion Mass Spectrometry. 5. Molecule Radical Reactions Prior to Ionization under Negative Chemical Ionization Conditions. *Org. Mass. Spectrom.* **17**, 376–381 (1982)
- Her, G.-R., Dolnikowski, G.G., Throck Watson, J.: Hydrogen Radical/Molecule Reactions in the Negative-Ion Mass Spectrometry of Dicyanomethane Derivatives of 9-Fluorenone and Benzophenone. *Org. Mass. Spectrom.* **21**, 329–334 (1986)
- Tumanskii, B., Kalina, O.: Radical Reactions of Fullerenes and Their Derivatives. *Developments in Fullerene Science*, 2, p. 25. Kluwer Academic Publishers, Dordrecht (2001)
- McEwen, C.N., McKay, R.G., Larsen, B.S.: C_{60} as a Radical Sponge. *J. Am. Chem. Soc.* **114**, 4412–4414 (1992)
- Lyakhovetsky, Y.I., Shilova, E.A., Tumanskii, B.L., Usatov, A.V., Avetysian, E.A., Sterlin, S.R., Pleshkova, A.P., Novikov, Y.N., Nekrasov, Y.S., Taylor, R.: Trifluoromethylation of [60]- and [70] Fullerene in the Ionization Chamber of a Mass Spectrometer. *Fuller. Sci. Technol.* **7**, 263–287 (1999)
- Lyakhovetsky, Y.I., Bashilov, V.V., Efanova, T.V., Shilova, E.A., Sokolov, V.I., Nekrasov, Y.S., Taylor, R.: Trifluoromethylation of C_{60} and C_{70} with Mercury(II) Trifluoroacetate. *Fuller. Nanotub. Carbon Nanostruct.* **17**, 85–98 (2009)
- Lyakhovetsky, Y.I., Shilova, E.A., Bashilov, V.V., Sokolov, V.I., Nekrasov, Y.S., Tumanskii, B.L.: Homolytic Reactive Mass Spectrometry of Fullerenes: Interaction of C_{60} and C_{70} with Organo- and Organoelement Mercurials in the Electron Impact Ion Source of a Mass Spectrometer; EPR, CIDEP, and MS Studies of Several Analogous Reactions of C_{60} Performed in Solution. *J. Phys. Chem. A* **113**, 13700–13710 (2009)
- Sukharev, Y.N., Sizoi, V.F., Nekrasov, Y.S.: The Computer Processing and Interpretation of Mass Spectral Information. VI. Computing the Isotopic Spectrum of Assumed Composition. *Org. Mass. Spectrom.* **16**, 23–25 (1981)
- Tumanskii, B.L., Kalina, O.G., Bashilov, V.V.: EPR Study of Radical Reactions of Fullerenes and Their Derivatives. *Mol. Mater.* **13**, 23–30 (2000)
- Makarov, V.I., Polak, L.S.: Excited and Superexcited Electronic States of Atoms and Molecules and Their Role in Radiation Chemistry. *Khim. Vys. Energ.* **4**, 3–23 (1970) [*High Energy Chem.* **4**, 1 (1970) (Eng. Transl.)]
- Bohme, D.K.: Buckminsterfullerene Cations: New Dimensions in Gas Phase Ion Chemistry. *Mass Spectrom. Rev.* **28**, 672–693 (2009)
- Petrie, S., Javahery, G., Wincel, H., Wang, J.R., Bohme, D.K.: Gas-Phase Reactions of the Buckminsterfullerene Cations C_{60}^{+} , C_{60}^{2+} , and C_{60}^{3+} with Aldehydes, Ketones, Carboxylic Acids, and Esters. *Int. J. Mass Spectrom. Ion Process.* **138**, 187–208 (1994)
- Petrie, S., Bohme, D.K.: Laboratory Studies of Ion/Molecule Reactions of Fullerenes: Chemical Derivatization of Fullerenes within Dense Interstellar Clouds and Circumstellar Shells. *Astrophys. J.* **540**, 869–885 (2000)
- Liu, Z., Hao, G., Guo, X., Liu, S.: Gas Phase Acetylation of C_{60} and C_{70} by Ion/Molecule Reactions. *Rapid Commun. Mass Spectrom.* **9**, 213–214 (1995)
- Guo, X., Liu, Z., Xu, W., Liu, S.: Gas-Phase Ion–Molecule Reactions of C_{60} and Theoretical Studies of $[C_{60}C_2H_3O]^+$ Adduct Cations. *J. Mass Spectrom.* **32**, 241–246 (1997)
- Sun, D., Liu, Z., Liu, Zh, Guo, X., Hao, C., Xu, W., Liu, S.: Gas Phase Derivations of Endohedral Metallofullerenes by Ion–Molecular Reactions. *Fuller. Sci. Technol.* **5**, 1461–1477 (1997)
- Einführung in die Photochemie von Einem Autorencollective: Veb Deutscher Verlag der Wissenschaften, Berlin, (1976) [pp. 167–172. Izdatelstvo Khimia, Leningrad (1976) (Russ. Transl.)]
- Krusic, P.J., Wasserman, E., Keizer, P.N., Morton, J.R., Preston, K.F.: Radical Reactions of C_{60} . *Science* **254**, 1183–1185 (1991)
- Morton, J.R., Negri, F., Preston, K.F.: Addition of Alkyl Radicals to C_{60} . Part 3. The EPR Spectra of R_3C_{60} Radicals and a Theoretical Study of HC_{60} and H_3C_{60} Radicals. *Can. J. Chem.* **72**, 776–782 (1994)