m-Nitrobenzyl Alcohol Electrochemistry in Fast Atom Bombardment Mass Spectrometry

Johnny D. Reynolds,* Kelsey D. Cook, James L. E. Burn,†
and Clifton Woods
Department of Chemistry, University of Tennessee, Knoxville, Tennessee, USA

The efficacy of m-nitrobenzyl alcohol (NBA) as a solvent (matrix) for fast atom bombardment (FAB) mass spectrometry of a group of pyrazolate-bridged dirhodium A-frame complexes has been assessed. Although NBA is frequently used to mitigate the formation of artifacts in FAB/MS of organometallics and other materials susceptible to bombardment-induced reactions, substantial evidence indicates that such reactions cause the formation of artifacts in the spectra obtained here. Parallel absorption spectroscopic studies have established that NBA is capable of inducing both *oxidation* and *reduction* reactions independent of ion bombardment, depending on analyte reduction half-wave potential ($E_{1/2}$). From the known electrochemistry of the complexes studied, it can be estimated that 1020 mV > $E_{1/2}$ > 500 mV for the reaction of NBA serving as a reducing agent, while 500 mV > $E_{1/2}$ > 424 mV for the reduction potential of NBA. However, in the presence of bombardment the former $E_{1/2}$ must be at least as low as 356 mV, and the latter $E_{1/2}$ must be at least as high as 1188 mV. The kinetics of redox reactions involving NBA, and therefore their influence on the appearance of FAB mass spectra, will be highly sample-dependent. However, this study illustrates an important potential role for redox reactions when NBA is used as a solvent, especially in the presence of bombardment in FAB/MS. Although analyte reaction products could be identified, substantial efforts aimed at identifying NBA oxidation and reduction products did not yield any definitive results due to the complexity of product mixtures. (*J Am Soc Mass Spectrom* 1992, 3, 113-121)

The choice of matrix [1-14] can have a dramatic effect on the appearance of fast atom bombardment (FAB) [15] mass spectra. Important matrix properties that can affect spectral quality and appearance include viscosity [16-18], dielectric constant (which affects ion pairing [19-32]), solvation [33, 34], and redox chemistry [10, 35-41].

For FAB mass spectrometry of inorganic and organometallic complexes, m-nitrobenzyl alcohol (NBA) often provides better overall sensitivity than the more commonly used glycerol matrix [10-12]. NBA can also reduce spectral complications that arise from bombardment-induced reactions [2, 39]. This latter benefit probably derives at least in part from the electrochemical properties of NBA. This electrochemistry, like that of most organic solvents, is highly irreversible, and often involves multiple electron transfer and/or rearrangement reactions [42]. Thus, although knowledge of this matrix chemistry could clarify our understanding of the FAB ionization process, monitoring it with normal electrochemical probes

is very difficult, if not impossible. This study seeks to investigate the intrinsic and bombardment-induced redox behavior of NBA in FAB/MS by a bracketing approach [9] for a series of pyrazolate-bridged dirhodium A-frame complexes, $M(PF_6)_n$, where $n = 1$ or 2, and M is the cation represented by Structure I [43, 44]. The complexes contain an apex pyrazolate anion (Z), and various transoid bridging (EE') and terminal (L) ligands (Table 1 and Structure I). One of the central Rh atoms may be in either the 1 + or 2 + nominal oxidation state, Rh(I) and Rh(II), respectively, while the other is always nominally Rh(I). In both cases, the two metals have been shown to be crystallographically equivalent [43]. Taken together, these features provide a wide range of redox potentials suitable for "bracketing" the redox potential of NBA, as was earlier demonstrated for the FAB matrix glycerol using bipyridyl complexes [9].

Experimental

FAB mass spectra were obtained with a ZAB-EQ mass spectrometer (VG Instruments, Manchester, UK) operating at an accelerating potential of 8 kV with a mass resolution of at least 2000 (10% valley). Research

*Current address: Ciba-Geigy Corp., Greensboro, NC 27419-8300.
†Current Address: Bechtel Corp., Oak Ridge, TN 37831.
Address reprint requests to Kelsey D. Cook, Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600.

Structure I
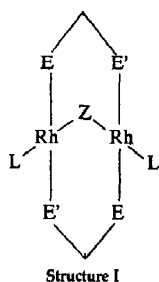
grade xenon (MG Industries, North Branch, NJ) was used with an Ion Tech (Middlesex, UK) ion gun, operating at an emission current of 1.0 mA and a potential of 8.0 kV. A thin film (5–10 μL) of a standard 10 mM solution of a complex was applied to a brass FAB probe tip [2]. Solutions were not degassed before analysis, but spectra were obtained only after emission had stabilized (typically after 1 min of bombardment). Spectra were then collected by summing data from 9 or 16 magnet scans over a period of 1–3 min. The reported results represent averages (normalized to 100%) of at least three such spectra (27 or 48 total scans), each obtained with a fresh sample. For all mass spectral data, the reported uncertainties represent the standard deviation of the mean $(s/N^{1/2})$ of N (at least three) replicates. Variance in the reported intensity of the base peak reflects the scan-to-scan variation in absolute intensities.

Electron ionization (EI) and methane chemical ionization (CI) mass spectra were obtained with a VG Instruments 70-SEQ mass spectrometer operating at an acceleration potential of 8 kV, at a source temperature of 200 °C, and with a mass resolution of at least 1000 (10% valley definition). For CI/MS, the source

Table 1. Pyrazolato-bridged dirhodium complexes of the general formula $[Rh_2(X, Y)Z(EE')_2L_2](PF_6)_n$ [a]

Complex	(X,Y)	EE'[b]	L[c]	n
1	(I, I)	PP	RNC	1
2	(I, I)	PP	CO	1
3	(I, I)	PA	RNC	1
4	(I, I)	PA	CO	1
5	(I, I)	AA	RNC	1
6	(I, I)	AA	CO	1
7	(I, II)	PP	RNC	2
8	(I, II)	PP	CO	2
9	(I, II)	PA	RNC	2
10	(I, II)	PA	CO	2
11	(I, II)	AA	RNC	2

[a] (X,Y) refers to the nominal oxidation state of the central metal atoms; Z = 4-bromo-3,5-dimethylpyrazolate anion.
[b] PP, bis(diphenylphosphino)methane; PA, (diphenylphosphino)(diphenylarsino)methane; AA, bis(diphenylarsino)methane.
[c] RNC, tert-butyl isocyanide; CO, carbon monoxide.

ion gauge pressure was $\sim 1 \times 10^{-4}$ torr. A Hewlett-Packard (Palo Alto, CA) model 5890 gas chromatograph (GC) with a 15 m × 0.25 mm × 0.25 μm (film thickness) DB-Wax column (J & W Scientific, Rancho Cordova, CA) was interfaced to the mass spectrometer and was operated at a He carrier gas flow rate of ~ 1 mL/min with a column head pressure of 7 psi. The GC temperature program started at 110 °C for 0.5 min, increased by 15 °C/min to 220 °C, then remained at 220 °C for 10 min. The GC was operated in a split injection mode with a split ratio of $\sim 10:1$. 1 μL injections of the following acetone solutions were employed: (1) 1.5 mM complex; (2) 0.15 M NBA; and (3) 1.5 mM complex and 0.15 M NBA. The last solution was prepared by mixing the complex and NBA, then allowing any reaction to proceed for at least 30 min prior to dilution with acetone. Most EI/CI GC/MS solutions also contained 1.7 mM methyl stearate as an internal standard.

Ultraviolet-visible (UV-Vis) absorption spectra were obtained by using a Hewlett-Packard model 8452 diode array spectrophotometer. Spectra of standard 0.3–3.4 mM (depending upon solubility) solutions of the complexes in methylene chloride ($MeCl_2$) or NBA were obtained with the corresponding pure solvent as reference. Solutions were generally run without degassing, except where noted. The cell path length was 0.1 cm.

Fourier transform infrared (FTIR) spectra were obtained with a Digilab (Cambridge, MA) FTS-7 FTIR spectrophotometer. A 2 M solution of a complex in NBA was allowed to react for at least 30 min, with occasional stirring. This solution was then added to 1 mL of $MeCl_2$, which had been degassed by bubbling with N_2 for at least 10 min. A portion of the $MeCl_2$ solution (≈ 100 μL) was applied to a NaCl window while concurrently evaporating the solvent with an Ar gas stream until the window was covered with analyte. The NaCl window was transferred into a N_2 atmosphere inside the FTIR chamber. Neat NBA and complex reference spectra were also obtained using a $MeCl_2$ intermediate solvent as indicated above.

The dirhodium complexes were synthesized, isolated, and purified by methods described elsewhere [43, 44]. All other chemicals were reagent grade and were used as received, except as noted.

Results and Discussion

Complexes 1 and 7 comprise a typical redox conjugate pair nominally differing only in the formal oxidation state of one of the Rh atoms (and a corresponding number of PF_6^- counterions; Table 1), which will be designated as Rh(I, I) and Rh(I, II) complexes, respectively. FAB spectra (Figure 1) for *both* members of this pair were dominated by the singly charged molecular cation (M^+), which would be expected for the Rh(I, I) complex but not the Rh(I, II) complex. In
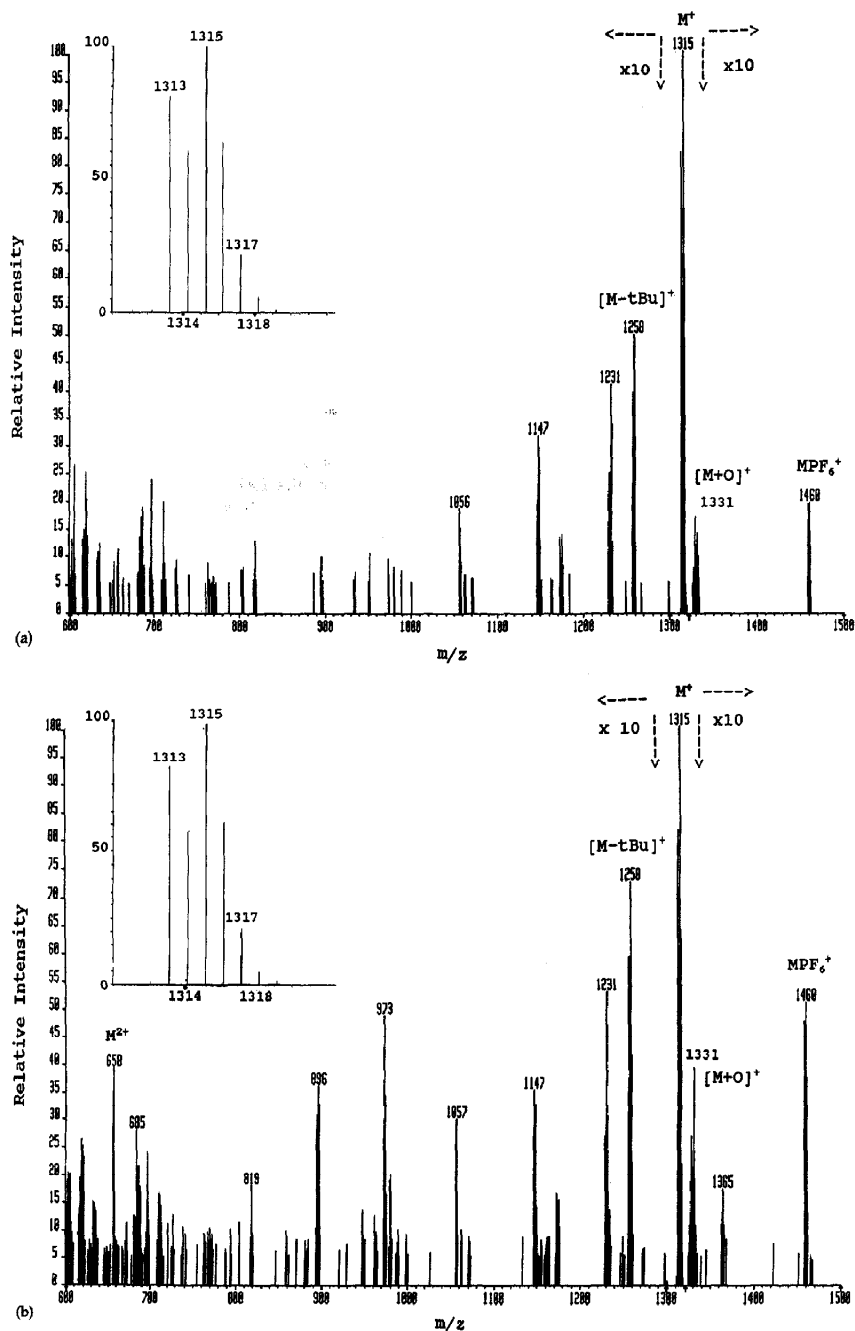
Figure 1. FAB mass spectra of a 10 mM solution of (a) *1* and (b) *7* in NBA. t-Bu represents a tertiary butyl group.

fact, M^+ was the base peak in the FAB spectrum for each of the eleven complexes (Table 2), *regardless of the nominal oxidation state of the Rh atoms.* The observed isotope patterns for these ions (M^+; see insets to Figure 1) match theoretical patterns well. Other ions detected in the spectra of most complexes include two Rh(I, II) ions (M^{2+}, with charge confirmed by isotope satellites separated by 0.5 u; and MPF_6^+), plus numerous fragments similar to those observed in Figure 1. Although the abundance of all fragment ions was low, these ions can provide some insight into structural effects on complex lability. Details of these fragmentation reactions can only be discerned by comparing FAB/MS and collision-induced dissociation (CID) tandem mass spectrometry (MS/MS) spectra of these and other complexes. These studies are beyond the scope of the present discussion and will be described completely in a subsequent publication.

Observation of Rh(I, I) ions in the FAB mass spectra of *7–11* and of Rh(I, II) ions in the FAB mass spectra of *1–6* provides evidence of either an electrochemical transformation or sample contamination. For all but *6*, the latter possibility can be ruled out on the basis of UV-Vis spectra. All 11 of these complexes are known to be reasonably stable in $MeCl_2$ solutions [43]. UV-Vis data for redox conjugate pairs (e.g., *1* and *7*, *2* and *8*, etc.) in $MeCl_2$ solutions illustrate that each Rh(I, I) complex has a significantly longer λ_{max} value (~ 490 nm) than the corresponding Rh(I, II) complex (~ 430 nm; Table 3). λ_{max} values for the 11 complexes in $MeCl_2$ solutions (Table 3) compare well with those reported by Woods et al. [43], confirming that the samples are not substantially contaminated by their redox conjugates. The Rh(I, II) analogue of *6* can be formed by bulk electrolysis, but it cannot be isolated from solution (possibly due to its high reduction potential; see below). Cyclic voltammetry showed that, like the other complexes, *6* was also reasonably pure [43].

Table 2. Relative intensities of selected ions detected in the FAB mass spectra of complexes *1–11*[a]

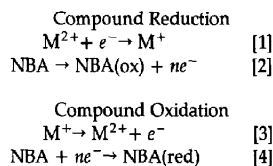| Complex	Detected ion		
	MPF_6^+	M^+	M^{2+}
1	2.1 ± 0.2	100.0 ± 5.8	—
2	7.9 ± 0.3	100.0 ± 7.1	—
3	2.9 ± 0.2	100.0 ± 5.4	—
4	6.2 ± 0.3	100.0 ± 6.2	—
5	5.0 ± 0.3	100.0 ± 3.9	—
6	6.2 ± 0.5	100.0 ± 4.7	—
7	6.3 ± 0.4	100.0 ± 4.9	3.7 ± 0.2
8	—	100.0 ± 8.5	—
9	5.9 ± 0.4	100.0 ± 9.2	3.3 ± 0.3
10	—	100.0 ± 5.2	—
11	14.2 ± 1.1	100.0 ± 6.0	7.1 ± 0.5

[a]Intensity is relative to the most abundant ion in the spectrum and refers to the most abundant ion in each isotope cluster.

Table 3. λ_{max} values for solutions of complexes *1–11* in $MeCl_2$ and NBA

Complex	Redox conjugate	λ_{max} in $MeCl_2$ (nm)	λ_{max} in NBA (nm)
1	7	508	430, 514
2	8	488	494
3	9	502	436, 504
4	10	484	486
5	11	495	497
6	—[a]	473	473
7	1	427	430
8	2	428	494
9	3	433	436
10	4	432	486
11	5	436	438

[a]Redox conjugate complex is not available (see text).

In the absence of contamination, the conjugate ions detected in the FAB mass spectra must arise from redox chemistry. Barring disproportionation (which should be energetically unfavorable), reactions involving the complexes could proceed with solvent as represented below:

$$\text{Compound Reduction}$$
$$M^{2+} + e^- \rightarrow M^+ \qquad [1]$$
$$NBA \rightarrow NBA(ox) + ne^- \qquad [2]$$

$$\text{Compound Oxidation}$$
$$M^+ \rightarrow M^{2+} + e^- \qquad [3]$$
$$NBA + ne^- \rightarrow NBA(red) \qquad [4]$$

Here, NBA (ox) and NBA (red) refer to undetermined solvent oxidation and reduction products, respectively (see below), and M^{2+} and M^+ refer to the molecular cations associated with the Rh(I, II) and Rh(I, I) complexes, respectively.

To assess the redox properties of NBA and its usefulness as a FAB matrix, it is of interest to determine whether these reactions occur spontaneously or are bombardment-induced for the various analytes. To test for spontaneous reaction, UV-Vis spectra were obtained for solutions that contained each of the 11 complexes and NBA (Table 3). For seven of these complexes, λ_{max} of NBA solutions resembled those for $MeCl_2$ solutions (for example, see spectra for *2* in Figure 2a). For two exceptional Rh(I, II) complexes, *8* and *10*, spectra of NBA solutions closely matched those of the corresponding redox conjugate (*2* and *4*, respectively; compare the UV-Vis spectra of NBA solutions of *2* and *8* in Figure 2 a and b, respectively). Since there was no appreciable solvatochromism affecting the seven "stable" complexes, it is reasonable to assert that the reaction of *8* and *10* with NBA to yield *2* and *4*, respectively, proceeds spontaneously in NBA via Reactions 1 and 2 above. These spontaneous reactions appear to proceed instantaneously, as
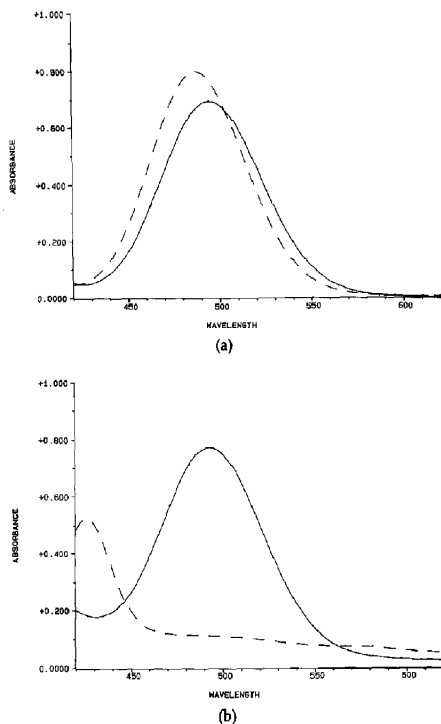
(a)

(b)

Figure 2. UV-Visspectra of (a) 0.6 mM *2* in methylene chloride (- - -) and 1.7 mM *2* in NBA (—); and (b) 0.6 mM *8* in methylene chloride (- - -) and 1.1 mM *8* in NBA (—).

UV-Vis measurements were made very soon after sample preparation. Similar spontaneous reduction has been reported for various complexes in glycerol [9], but we are unaware of a corresponding report of spontaneous analyte reduction by NBA. This observation may not be surprising in light of the high reduction half-wave potentials ($E_{1/2}$) of *8* and *10* (Table 4). Among the complexes studied, only the unstable redox conjugate of *6* [*6*(ox)] has a higher $E_{1/2}$. Although quantitative comparison of $E_{1/2}$ values can be complicated by solvent effects, review of the data of Tables 3 and 4 suggests a rough range of 1020 mV > $E_{1/2, \text{NBA(ox)}}$ > 500 mV for the reverse of Reaction 2.

The other two complexes for which UV-Vis $\lambda_{\max}$ values show solvent dependence are Rh(I, I) complexes (*1* and *3*; Table 3), which correspond to the most easily oxidized complexes (Table 4). The UV-Vis spectra of *1* and *3* indeed appear to reflect at least partial spontaneous oxidation by NBA (e.g., compare the UV-Vis spectra of NBA solutions of *1* and *7* in Figure 3, a and b, respectively.) By reasoning analogous to that above, $E_{1/2, \text{NBA}}$ for reaction 4 can be bracketed within the rather narrow limits of 500 mV > $E_{1/2, \text{NBA}}$ > 424 mV (Table 4).

The possibility of air-induced oxidation due to residual O_2 in the NBA solvent was tested by bubbling the solvent with N_2 for at least 10 min to remove O_2 prior to adding the analyte. UV-Vis spectra of degassed and undegassed NBA solutions of all 11 samples were identical.

It is important to note that while UV-Vis spectra provide strong evidence of spontaneous reduction of *8* and *10* (and spontaneous oxidation of *1* and *3*), the corresponding FAB/MS spectra (Table 2) suggest that reactions other than simple analyte redox reactions may have occurred. For example, under bombardment conditions the product of reducing *10* in NBA is *not* identical to *4* in NBA; MPF_6^+ is detected only in the spectrum of the latter compound. Differences are also evident in the CID MS/MS spectra of the corresponding M^+ ions [45]. These differences are most likely attributable to structural (isomeric) and/or energetic differences between "native" and matrix-reduced or -oxidized materials. Further studies to assess this chemistry more thoroughly are on-going.

In addition to the intrinsic redox chemistry of NBA reflected in Table 4, there is evidence of bombardment-induced redox changes. While only the complexes of highest $E_{1/2}$ (*8* and *10*) were reduced *spontaneously*, the other three Rh(I, II) complexes experienced bombardment-induced reduction (Table 2), including even that with the *lowest* $E_{1/2}$(*7*). This suggests that *under bombardment conditions*, the "effective matrix $E_{1/2}$" for the reverse of Reaction 2 (possibly reflecting the reactivity of free electrons released upon bombardment [4, 7]) must be at least as low as 356 mV. There is also evidence for *bombardment-induced oxidation*, a much more uncommon phenomenon [40]. Detection of Rh(I, II) ions (MPF_6^+) for all six of the Rh(I, I) complexes (Table 2) suggests that the "effective matrix $E_{1/2}$" for Reaction 4 *under bombardment conditions* is at least as high as 1188 mV.

Finally, attempts were made to identify the NBA redox products [NBA(ox) and NBA(red); see reactions 2 and 4, respectively]. Preliminary EI and CI GC/MS analyses of a solution containing NBA in acetone revealed four "impurities" (Table 5), which remained even after recrystallization of NBA from an ether/hexane solution. Reasonable candidates for NBA(ox) (*m*-nitrobenzaldehyde) and NBA(red) (*m*-aminobenzyl alcohol) were included among these impurities. All impurities were confirmed by library search and/or by retention time matching with a 1.5 mM solution of the respective standard material in acetone.

Methyl stearate was used as an internal standard to test for changes in relative abundances (*i*) of the impurity components upon reaction of NBA with one of the reactive complexes (*1*, *3*, *8*, and *10*):

$$i = i_A / i_S$$

where i_A and i_S represent the peak areas from reconstructed EI or CI GC/MS ion chromatograms for an ion (Tables 5 and 6) representative of the species of

Table 4. Redox half-reactions for complexes *1-11* and NBA

Reaction[a]	Potential (mV)[b]	Comment
$6(ox) + e^- \rightarrow 6$	1188	Bombardment-induced oxidation is observed for *6*
$10 + e^- \rightarrow 4$	1126	Matrix-induced reduction is observed for *10*; bombardment-induced oxidation is observed for *4*
$8 + e^- \rightarrow 2$	1020	Matrix-induced reduction is observed for *8*; bombardment-induced oxidation is observed for *2*
$NBA(ox) + ne^- \rightarrow NBA$	$1020 > E_{1/2} > 500$	
$11 + e^- \rightarrow 5$	500	Bombardment-induced reduction is observed for *11*; bombardment-induced oxidation is observed for *5*
$NBA + ne^- \rightarrow NBA(red)$	$500 > E_{1/2} > 424$	
$9 + e^- \rightarrow 3$	424	Matrix-induced oxidation is observed for *3*; bombardment-induced reduction is observed for *9*
$7 + e^- \rightarrow 1$	356	Matrix-induced oxidation is observed for *1*; bombardment-induced reduction is observed for *7*

[a] See text and Table 1 for definitions.
[b] Data for complexes from ref 43.

interest (impurity or NBA) and of the methyl stearate standard, respectively. The *i* for NBA decreased when a reactive complex was mixed with NBA (relative to *i* for neat NBA; Table 6), indicating that a reaction between the complex and NBA had occurred. Furthermore, *i* for *m*-nitrobenzaldehyde [potentially NBA(ox)] increased as expected when an oxidizing complex (*8* or *10*) was mixed with NBA, as perhaps did *i* for *m*-aminobenzyl alcohol [potentially NBA(red)] when a reducing complex (*1* or *3*) was present with NBA. Unexpected and currently unexplained was the observed increase in *i* for *m*-nitrobenzaldehyde upon addition of a reducing complex (*1* or *3*) to NBA. The possibility that this increase results from thermally induced oxidation of NBA inside the hot (250 °C) GC injection port was tested by analyzing a NBA solution that contained a nonreactive complex (*7*). In this case, no significant change in *i* (compared with a solution that contained neat NBA) was detected for any of the four "impurities" monitored. Thus, it appears that the reducing complexes (*1* and *3*) have an active role in the oxidation of NBA. No significant changes in *i* for the other two impurities listed in Table 5 were detected for any of the complexes (*1, 3, 7, 8,* or *10*) tested (Table 6).

CI GC/MS analyses revealed three reaction products that were only detected when NBA and a reactive complex (*1, 3, 8,* or *10*) were *both* present in solution. One of these products (unknown *X*; Figure 4a) was observed when any one of the four reactive complexes was mixed with NBA. Unknown *Y* (Figure 4b) was observed only when one of the oxidizing complexes was mixed with NBA; similarly, one of the reducing complexes had to be present for observation of *Z* (Figure 4c). EI GC/MS spectra of all three "unknown" reaction products were very weak and contained only ions of low mass-to-charge ratio. Efforts to discern ion structures of these reaction products based upon the available mass spectral data (including high resolution analyses) were not successful. Further attempts to ascertain the identity of these reaction products by comparing FTIR spectra of NBA solutions with reactive (*1, 3,* or *8*) and corresponding unreactive (*7, 9,* or *2*) complexes were also inconclusive. The only differences evident upon spectral subtraction were small shifts in λ_{max} of the terminal ligands (carbon monoxide and tert-butyl isocyanide), which are sensitive to the metal oxidation state [43]. Evidently, the large molecular weight disparity between complex and solvent, the limited complex solubility and availability, and the high complex absorptivities preclude generation of solvent redox products in concentrations high enough for unambiguous identification by these methods.

Conclusions

Matrix- and bombardment-induced reductions in FAB/MS are becoming well-recognized reactions, which often can be mitigated by using NBA as the matrix. For the family of complexes studied here, we find that mitigation of the formation of reductive
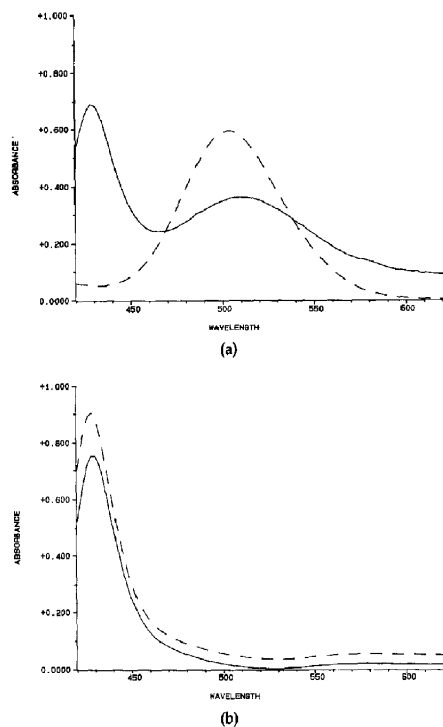
(a)

(b)

Figure 3. UV-Visspectra of (a) 0.4 mM *1* in methylene chloride (- - -) and 3.4 mM *1* in NBA (—); (b) 0.3 mM *7* in methylene chloride (- - -) and 0.3 mM *7* in NBA (—).

Table 5. Impurities found in the EI and CI GC/MS analyses of NBA

Component	Retention time (min)	Relative intensity[a] (m/z)
m-Nitrobenzaldehyde	6.7	0.080 (151)
Methyl stearate[b]	7.3	0.073 (298)
m-Aminobenzaldehyde	7.8	0.003 (121)
o-Nitrobenzyl alcohol	8.7	0.010 (135)
m-Aminobenzyl alcohol	9.2	0.019 (123)
m-Nitrobenzyl alcohol	10.9	1.000 (153)

[a] Based upon peak areas from reconstructed EI GC/MS ion chromatograms for the mass-to-charge ratio indicated.
[b] Added as an internal standard.

artifacts is somewhat limited. In fact, we find that NBA (like glycerol) is capable of inducing analyte reduction, with and without bombardment. Furthermore, evidence also supports the formation of *spontaneous oxidative* artifacts in NBA, which have not been prominently noted previously. Although these observations should not be surprising, they do reemphasize the prevasive importance of matrix chemistry in FAB/MS.

Acknowledgments

Table 6. Relative abundances (i)[a] of selected components in various solutions

Component	NBA	1 + NBA	3 + NBA	7 + NBA	8 + NBA	10 + NBA
			Solutions			
m-Nitrobenzaldehyde	1.1 ± 0.1	1.5 ± 0.1	2.0 ± 0.1	1.2 ± 0.1	1.8 ± 0.1	2.2 ± 0.1
m-Amino-benzaldehyde	0.041 ±0.003	0.038 ±0.002	0.040 ±0.003	0.039 ±0.003	0.040 ±0.002	0.042 ±0.003
o-Nitrobenzyl alcohol	0.14 ± 0.01	0.13 ± 0.01	0.12 ± 0.01	0.14 ± 0.01	0.12 ± 0.01	0.13 ± 0.01
m-Aminobenzyl alcohol	0.26 ± 0.01	0.29 ± 0.01	0.27 ± 0.01	0.25 ± 0.01	0.25 ± 0.01	0.26 ± 0.01
m-Nitrobenzyl alcohol	13.7 ± 0.4	9.4 ± 0.1	12.0 ± 0.2	13.2 ± 0.3	9.2 ± 0.3	10.0 ± 0.3
Unknown X[b]	—[c]	0.014 ±0.001	0.018 ±0.001	—[c]	0.085 ±0.004	0.092 ±0.006
Unknown Y[d]	—[c]	—[c]	—[c]	—[c]	0.0030 ±0.0003	0.0040 ±0.0002
Unknown Z[e]	—[c]	0.0020 ±0.0002	0.0030 ±0.0002	—[c]	—[c]	—[c]

[a] See text for definitions. i data based upon peak areas from reconstructed EI GC/MS ion chromatograms for the mass to charge ratio indicated in Table 5 unless otherwise noted.
[b] i is based upon CI data with i_A and i_S for m/z 194 and 299, respectively.
[c] Not detected.
[d] i is based upon CI data with i_A and i_S for m/z 178 and 299, respectively.
[e] i is based upon CI data with i_A and i_S for m/z 198 and 299, respectively.
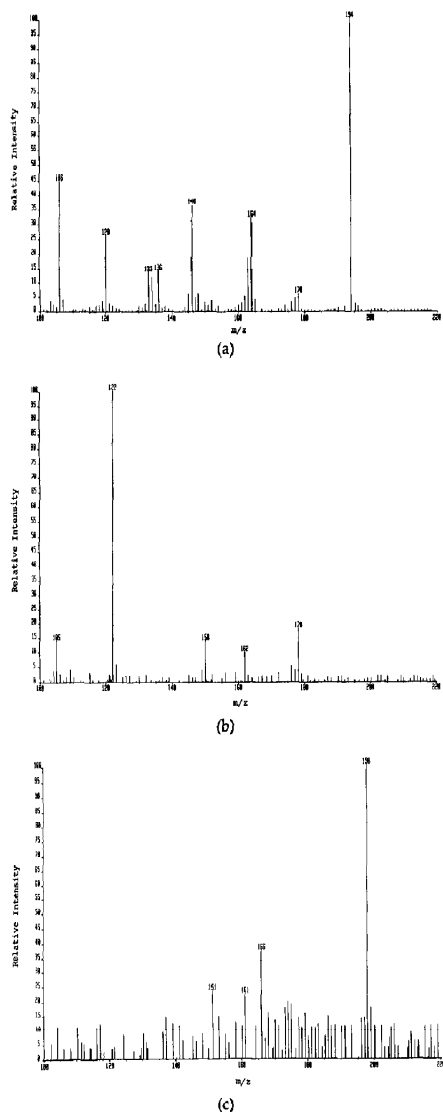
(a)

(b)

(c)

Figure 4. CI GC mass spectra of reaction products (a) X (retention time = 9.7 min from NBA and *1, 3, 8,* or *10*); (b) Y(retention time = 6.8 min from NBA and *8* or *10*); and (c) Z (retention time = 5.9 min from NBA and *1* or *3*).

References

1. De Pauw, E. *Mass Spectrom. Rev.* **1986**, *5*, 191.
2. Reynolds, J. D.; Cook, K. D. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 149.
3. Keough, T. *Int. J. Mass Spectrom. Ion Processes* **1988**, *86*, 155.
4. Miller, J. M.; Balasanmugam, K.; Nye, J.; Deacon, G. B.; Thomas, N. C. *Inorg. Chem.* **1987**, *26*, 560.
5. Kyranos, J. N.; duSorbier, B. M.; Wronka, J.; Vouros, P.; Kirby, D. P. *Org. Mass Spectrom.* **1988**, *23*, 443.
6. Musselman, B.; Watson, J. T. *Biomed. Environ. Mass Spectrom.* **1987**, *14*, 247.
7. Williams, D. H.; Findeis, A. F.; Naylor, S.; Gibson, B. W. *J. Am. Chem. Soc.* **1987**, *109*, 1980.
8. Takayama, M.; Fukai, T.; Nomura, T. *Int. J. Mass Spectrom. Ion Processes* **1989**, *89*, R1.
9. Callahan, J. H.; Hool, K.; Reynolds, J. D.; Cook, K. D. *Anal. Chem.* **1988**, *60*, 714.
10. Miller, J. M. *Mass Spectrom. Rev.* **1990**, *9*, 319.
11. Mallis, L. M.; Scott, W. J. *Org. Mass Spectrom.* **1990**, *25*, 415.
12. Barber, M.; Bell, D.; Eckersley, M.; Morris, M.; Tetler, L. *Rapid Commun. Mass Spectrom.* **1988**, *2*, 18.
13. Nedderman, A. N. R.; Williams, D. H. *Biological Mass Spectrom.* **1991**, *20*, 289.
14. Aubagnac, J. L. *Rapid Commun. Mass Spectrom.* **1990**, *4*, 114.
15. Barber, M.; Bordoli, R. S.; Sedgwick, R. D.; Tyler, A. N. *J. Chem. Soc. Chem. Commun.* **1981**, 325.
16. Sunner, J. A.; Morales, A.; Kebarle, P. *Int. J. Mass. Spectrom. Ion Processes* **1989**, *87*, 287.
17. Sunner, J. A.; Morales, A.; Kebarle, P. *Anal. Chem.* **1988**, *60*, 98.
18. Dube, G.; Vollhardt, D. *Org. Mass Spectrom.* **1990**, *25*, 404.
19. Reynolds, J. D.; Cook, K. D. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 233.
20. Reynolds, J. D.; Cook, K. D. *Int. J. Mass Spectrom. Ion Processes* **1990**, *97*, 325.
21. Callahan, J. H.; Hool, K.; Reynolds, J. D.; Cook, K. D. *Int. J. Mass Spectrom. Ion Processes* **1987**, *75*, 291.
22. Ligon, W. V. Jr.; Dorn, S. B. *Int. J. Mass Spectrom. Ion Processes* **1985**, *63*, 315.
23. Ligon, W. V. Jr.; Dorn, S. B. *Int. J. Mass Spectrom. Ion Processes* **1986**, *68*, 337.
24. De Pauw, E.; Pelzer, G.; Dung, D. V.; Marien, J. *Biomed. Biophys. Res. Commun.* **1984**, *123*, 27.
25. Hand, O. W.; Scheifers, S. M.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1987**, *78*, 131.
26. Ligon, W. V. Jr.; Dorn, S. B. *Int. J. Mass Spectrom. Ion Processes* **1984**, *57*, 75.
27. Ligon, W. V. Jr.; Dorn, S. B. *Int. J. Mass Spectrom. Ion Processes* **1987**, *78*, 99.
28. Ligon, W. V. Jr.; Dorn, S. B. *Int. J. Mass Spectrom. Ion Processes* **1984**, *61*, 113.
29. Ligon, W. V. Jr.; Dorn, S. B. *Anal. Chem.* **1985**, *57*, 1993.
30. Ligon, W. V. Jr.; Dorn, S. B. *Fresenius Z. Anal. Chem.* **1986**, *325*, 626.
31. Shiea, J.; Sunner, J. *Org. Mass Spectrom.* **1991**, *26*, 38.
32. Todd, P. J. *Org. Mass Spectrom.* **1988**, *23*, 419.
33. Fraefel, A.; Seibl, J. *Mass Spectrom. Rev.* **1985**, *4*, 151.
34. Wysocki, V. H.; Kenttamaa, H. I.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1987**, *75*, 181.
35. Vekey, K. *Int. J. Mass Spectrom. Ion Processes* **1990**, *97*, 265.
36. Pelzer, G.; De Pauw, E.; Dung, D. V.; Marien, J. *J. Phys. Chem.* **1984**, *88*, 5065.
37. Cerny, R. L.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 1160.
38. Santana-Marques, M. G. O.; Ferrer-Correia, A. J. V.; Gross, M. L. *Anal. Chem.* **1989**, *61*, 1442.

39. Kyranos, J. N.; Vorous, P. *Biomed. Environ. Mass Spectrom.* **1990**, *19*, 628.
40. Prokai, L.; Hsu, B.-H.; Farag, H.; Bodor, N. *Anal. Chem.* **1989**, *61*, 1723.
41. Aubagnac, J. L.; Clarmont, R. M.; Sanz, D. *Org. Mass Spectrom.* **1990**, *25*, 293.
42. Sundholm, G. J. *Electroanal. Chem.* **1971**, *31*, 265.

43. Woods, C.; Tortorelli, L. J.; Rillema, D. P.; Burn, J. L. E.; DePriest, J. C. *Inorg. Chem.* **1989**, *28*, 1673.
44. Janke, C. J.; Tortorelli, L. J.; Burn, J. L. E.; Tucker, C. A.; Woods, C. *Inorg. Chem.* **1986**, *25*, 4597.
45. Reynolds, J. D.; Burn, J. L. E.; Woods, C.; Cook, K. D. In *Proceedings 38th ASMS Conference on Mass Spectrometry and Allied Topics*; Tucson, AZ, June 3–8, 1990; p. 1431.