Anal. Chem. 1982, 54, 492–496

Nitric Oxide Chemical Ionization Mass Spectrometry of Alcohols

Donald F. Hunt,* T. Michael Harvey, William C. Brumley, James F. Ryan, III, and John W. Russell

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Electron ionization of nitric oxide at 1 torr affords the nitrosonium ion, NO^+, in high abundance. Under chemical ionization conditions, this ion undergoes a different set of ion–molecule reactions with primary, secondary, and tertiary alcohols. Reaction of NO^+ with primary and secondary alcohols affords abundant $(M - 1)^+$ and $(M - 2 + NO)^+$ ions. An $(M - 3)^+$ ion is generated from primary but not from secondary alcohols. Secondary but not usually primary alcohols afford $(M - OH)^+$ ions. Tertiary alcohols afford spectra containing a single ion corresponding to $(M - OH)^+$. Nitric oxide chemical ionization mass spectra can be used to differentiate isomeric alcohols.

In this report we describe the results of our investigation on the utility of nitric oxide as a reagent for obtaining chemical ionization mass spectra of alcohols. This work was undertaken to further our understanding of the gas-phase ion–molecule chemistry of the nitrosonium ion, NO^+, and as part of an effort to develop a sensitive analytical mass spectrometric technique suitable for the analysis of alcohols. Electron ionization (*1*) and both methane (*2*) and isobutane (*3*) chemical ionization mass spectrometry are unsatisfactory for this class of compounds since spectra obtained by these techniques are frequently devoid of ions characteristic of sample molecular weight and fail to contain information about the degree of substitution on the carbon bearing the hydroxyl group. Nitric oxide chemical ionization overcomes both of these problems.

Electron ionization of nitric oxide at 1 torr affords a mass spectrum in which 90% of the ion current is carried by the nitrosonium ion, NO^+. The remaining 10% of the ion current is divided about equally between the adduct ions, $(NO{\cdot}NO)^+$ and $(NO{\cdot}H_2O)^+$ at m/z 60 and 48, respectively. Previous work has shown that the ion–molecule chemistry of NO^+ can be employed to enhance the molecular ion abundance in the spectra of biologically important compounds (*4*) and their trimethylsilyl ether (*5*), for functional group identification in organic compounds (*6*) and for the analysis of saturated (*7*) and unsaturated (*8*) hydrocarbons. Reactions of the nitrosonium ion with a variety of organic molecules under ion cyclotron resonance conditions have been reported by Williamson and Beauchamp (*9*). The temperature dependence of hydride transfer between acetaldehyde and NO^+ (*10*) and the effect of vibrational and translational energy of NO^+ on hydride transfer from isobutane have also been studied (*11*). Here we discuss the energetics, mechanisms, and analytical applications of ion–molecule reactions involving NO^+ and alcohols.

EXPERIMENTAL SECTION

Chemicals and Reagent Gases. Nitric oxide (99.97%) and methane (99.97%) employed in this study were purchased from Matheson Gas Products, Inc., East Rutherford, NJ. Alcohol samples were obtained from Chemical Samples Co., Columbus, OH, or from Aldrich Chemical Co., Milwaukee, WI, and were used without further purification. Compounds **35–39** were prepared by reduction of methyl esters of the corresponding carboxylic acids with lithium aluminum deuteride obtained from Alfa Inorganics, Beverly, MA. Synthetic samples were purified by preparative gas chromatography.

Instrumentation. Chemical ionization mass spectra were recorded at a resolution of 2000, 10% valley, on an AEI-MS 902 double focusing mass spectrometer equipped with a chemical ionization ion source manufactured by Scientific Research Instruments, Inc., Baltimore, MD (*12*). Primary ionization of the chemical ionization reagent gas was accomplished by using either a Townsend discharge (*13, 14*) or a 500-eV beam of electrons from a heated rhenium filament. In the filament mode of operation, pressures for the reagent gas and sample were maintained at 0.5–1.0 torr and 10^{-3} torr, respectively. Filament lifetime in the presence of nitric oxide at 1 torr is ~6 h. Other operating parameters include an accelerating potential of 8 kV, an analyzer pressure of 3×10^{-7} torr, and a source temperature of 100–200 °C as measured by a thermocouple gauge. Spectra recorded with the Townsend discharge source were obtained at a nitric oxide pressure of 1 torr and the discharge operating in the anode mode (*13, 14*) at a voltage between 700 and 750 V and a current of 20–40 μA. Operation of the Townsend discharge is unaffected by oxidizing reagent gases at 1 torr.

Sample introduction was accomplished by one of three procedures. Gases and highly volatile liquids were metered through a fine needle valve into the reagent gas stream as it passed through an all-glass unheated inlet system. Higher boiling liquids were introduced from a capillary vial through a stainless steel needle valve and a 6 in. piece of glass-lined stainless steel tubing screwed directly into the source block. Solids were added via a direct insertion probe heated independently of the ion source.

RESULTS

Data obtained from nitric oxide chemical ionization mass spectra of primary, **1–17**, secondary, **18–26**, and tertiary alcohols, **27–33**, are presented in Table I. Product ions resulting from the reaction of NO^+ with alcohols **34–41**, labeled with deuterium on the α-carbon atom are summarized in Table II. In general we find that the nitrosonium ion functions as an electrophile, hydride abstractor, and hydroxide ion abstractor toward alcohols in the gas phase. Ions corresponding to electrophilic addition of NO^+ to aldehydes and ketones, $(M - 2 + NO)^+$, are also prominent in the nitric oxide chemical ionization mass spectra of primary and secondary alcohols, respectively. Of particular interest is the finding that NO^+ undergoes a different set of ion–molecule reactions with primary, secondary, and tertiary alcohols. Accordingly, nitric oxide chemical ionization mass spectrometry can be employed to differentiate isomeric alcohols. Reaction of NO^+ with primary and secondary alcohols affords abundant $(M - 1)^+$ and $(M - 2 + NO)^+$ ions. An $(M - 3)^+$ ion is generated from primary but not secondary alcohols. Secondary but usually not primary alcohols afford $(M - OH)^+$ ions. Tertiary alcohols afford spectra containing a single ion corresponding to $(M - OH)^+$.

DISCUSSION

Electrophilic Addition of NO^+. Electrophilic addition of NO^+ to an alcohol presumably affords an ion having a structure corresponding to a protonated alkyl nitrite, **42**, as shown in eq 1. Calculation of the enthalpy change for this

$$ROH + NO^+ \rightarrow \underset{\mathbf{42}}{ROHNO^+} \qquad (1)$$

reaction requires knowledge of either the proton affinity of the neutral nitrite or the heat of formation, ΔH_f, of the pos-

0003-2700/82/0354-0492$01.25/0

Table I. Nitric Oxide Chemical Ionization Mass Spectra of Alcohols

compound	no.	mol wt	% total sample ion current[a] $(M-1)^+$	$(M-2+NO)^+$	$(M-3)^+$	$(M-OH)^+$	$(M+NO)^+$	other (mass)
Primary Alcohols								
CH_3OH	**1**	32		32.4			46.5	21.1 (91)
C_2H_5OH	**2**	46	18.1	60.2	10.8		10.8	
n-C_3H_7OH	**3**	60	19.1	39.9	25.0		14.9	1.6 (91)
n-C_4H_9OH	**4**	74	17.2	31.3	31.3		20.1	
n-$C_5H_{11}OH$	**5**	88	13.1	33.8	37.6		15.4	
n-$C_6H_{13}OH$	**6**	102	15.9	30.6	31.8		15.2	5.7 (83)
n-$C_7H_{15}OH$	**7**	116	17.9	28.5	35.7		17.9	
n-$C_8H_{17}OH$	**8**	130	20.9	24.4	34.8		19.9	
n-$C_9H_{19}OH$	**9**	144	21.1	21.1	35.2		22.5	
n-$C_{10}H_{21}OH$[b]	**10**	158	29.8	29.8	33.1		7.2	
n-$C_{12}H_{25}OH$	**11**	186	14.5	17.4	58.1		9.9	
n-$C_{14}H_{29}OH$	**12**	214	17.5	16.4	58.5		7.6	
			38.7[c]	2.7[c]	55.2[c]		3.2[c]	3.3[c] (197)
$(CH_3)_3CCH_2OH$	**13**	88	11.9	59.5	8.9		4.8	14.9 (57)
n-$C_{18}H_{37}OH$[c]	**14**	270	49.3	0.5	32.0			13.3 (253)
n-$C_{22}H_{45}OH$[c]	**15**	326	48.3	0.5	43.5			4.8 (209)
n-$C_{24}H_{49}OH$[c]	**16**	354	40.0	0.9	48.5			4.1 (357)
$PhCH_2CH_2OH$	**17**	122					81.3	3.2 (91); 3.2 (105); 6.5 (122); 5.7 (139)
Secondary Alcohols								
c-C_4H_7OH	**18**	72	34.5	38.8		26.7		
c-C_5H_9OH	**19**	86	40.0	41.8		7.2		10.9 (67)
c-$C_6H_{11}OH$	**20**	100	30.7	48.8		9.8		3.1 (112); 7.7 (81)
c-$C_7H_{13}OH$	**21**	114	26.4	34.2		31.4		6.4 (95)
n-$C_3H_7(CH_3)CHOH$	**22**	88	46.2	39.6		14.2		
n-$C_6H_{13}(CH_3)CHOH$	**23**	130	35.5	52.1		12.5		
$C_3H_7CH(CH_3)CH(OH)CH(CH_3)_2$	**24**	144	34.4	17.1		19.5		6.9 (85); 15.5 (71); 6.6 (57)
$[C_2H_5CH(CH_3)]_2CHOH$	**25**	144	21.9	11.5		20.0		2.7 (102); 5.6 (86); 15.9 (85); 11.5 (71); 10.7 (57)
$(CH_3)_3CCH_2CHC(CH_3)_3OH$	**26**	144	16.6	4.9		3.2		1.6 (102); 4.2 (99); 36.7 (85); 4.2 (83); 8.6 (71); 20 (57)
Tertiary Alcohols								
$(CH_3)_3COH$	**27**	74				100.0		
$C_2H_5(CH_3)_2COH$	**28**	88				100.0		
$(CH_3)_2CH(C_4H_9)(CH_3)COH$	**29**[b]	144				100.0		
$[C_2H_5CH(CH_3)CH_2](C_2H_5)(CH_3)COH$	**30**[b]	144				100.0		
$[CH_3CH(CH_3)CH_2]_2(CH_3)COH$	**31**[b]	158				25.8		27.0 (85); 29.2 (71); 18.3 (57)
c-$C_3H_4(CH_3)OH$	**32**	100				100.0		
c-$C_6H_{10}(C_4H_9)OH$	**33**	156				100.0		

[a] Ion source temperature was 100 °C unless otherwise indicated. [b] Ion source temperature was 80 °C. [c] Ion source temperature was 230 °C.

Table II. Nitric Oxide Chemical Ionization Mass Spectra of Deuterium Labeled Alcohols

compound	no.	mol wt	% total sample ion current[a] $(M-2)^+$	$(M-4)^+$	$(M-5)^+$	$(M-3+NO)^+$	$(M+NO)^+$	other (mass)
CD_3OD	**34**	36				33.9[b]	42.8	23.3 (94)
$CH_3CH_2CD_2OH$	**35**	62	32.4	1.0	9.7	51.9	4.6	
$(CH_3)_2CHCD_2OH$	**36**	76	10.2	9.9	30.1	30.1		1.5 (118)
$(CH_3)_2CHCH_2CD_2OH$	**37**	90	5.7	6.8	30.6	35.6		11.4 (122); 10.0 (123)
$CH_3(CH_2)_4CD_2OH$	**38**	104	16.7	2.6	28.1	37.2		10.0 (146); 3.0 (160)
$CH_3(CH_2)_5CD_2OH$	**39**	118	15.8	7.5	28.3	37.7		10.6 (160)
$CH_3(CH_2)_8CD_2OH$	**40**	160	24.5	12.2	8.2	44.4		9.4 (202); 0.8 (216)
$HOCD_2(CH_2)_8CD_2OH$	**41**	178	18.2		27.2			13.6 (179); 22.7 (140); 13.6 (158); 4.5 (187)

[a] Ion source temperature was 100 °C. [b] $(M-4+NO)^+$.

itively charged product ion. Since these quantities have only been determined for methyl nitrite, we have attempted to estimate the enthalpy changes for ion–molecule reactions of the nitrosonium ion with other alcohols using the thermochemical values in Table III. Results of these estimations are presented in Table IV.

For electrophilic addition of NO^+ to alcohols, estimates for the changes in enthalpy range from −38 to −45 kcal mol^{-1} depending on the substitution pattern at the α-carbon atom in the sample molecule. Proton transfer from CH_5^+ to the same alcohols is more exothermic and occurs with an enthalpy change of −55 to −65 kcal mol^{-1}. Since the energy liberated

Table III. Thermochemical Values Employed To Estimate Enthalpy Changes in the Reactions of the Nitrosonium Ion with Alcohols

compound	ΔH°_{f298}, kcal mol^{-1}	PA[a]	compound	ΔH°_{f298}, kcal mol^{-1}
NO	+21.6[b]		H_2ONO^+	+163.5[k]
HNO	+31.7[c]		CH_3OHNO^+	+161[g]
HONO	−18.5[d]	184[f]	$C_2H_5OHNO^+$	+150[l]
CH_3ONO	−16.5[e]	187[g]	n-$C_3H_7OHNO^+$	+144[l]
C_2H_5ONO	−24.9[b]	191[h]	n-$C_4H_9OHNO^+$	+138[l]
n-C_3H_7ONO	−30.0[e]	192[h]	$(CH_3)_2CHOHNO^+$	+139[l]
n-C_4H_9ONO	−35.0[e]	193[h]	$(CH_3)_3COHNO^+$	+129[l]
$(CH_3)_2CHONO$	−33.7[e]	193[h]	CH_2ONO^+	+181.7[m]
$(CH_3)_3CONO$	−43.3[e]	194[h]	CH_3CHONO^+	+159.3[m]
$NHOH\cdot$	+30.0[i]		$C_2H_5CHONO^+$	+150.3[m]
NO^+	+239.9[j]		$(CH_3)_2CONO^+$	+138.4[m]

[a] Proton affinity defined as $-\Delta H$ for the reaction $R + H^+ \longrightarrow RH^+$. [b] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1. [c] Holmes, J. L. *Proc. Chem. Soc., London* **1962**, 75. [d] Ashmore, P. G.; Tyler, B. J. *J. Chem. Soc.* **1961**, 1017. [e] Estimated by the group additivity method: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976. [f] Estimated from data in Table III using the equation in footnote *a*. [g] McAllister, T.; Pitman, P. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 241–248. [h] Estimated from the PA of HONO by assuming that replacement of H by Me, Et, *n*-Pr, *n*-Bu, *i*-Pr, and *t*-Bu increases the PA by 12, 16, 17, 18, 18, and 19 kcal, respectively. [i] Estimated from the bond dissociation energy of NH_2OH, 60 kcal, and the group additivity method of Benson (footnote *e*). [j] Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970. [k] Estimated from the equation in footnote *a* and the enthalpy change for the reaction $H_2O + NO^+ \longrightarrow H_2ONO^+$, $\Delta H = -18.5$; French, M. A.; Hills, L. P.; Kebarle, P. *Can. J. Chem.* **1973**, *51*, 456–461. [l] Estimated from the equation in footnote *a* and data in Table III. [m] Estimated by assuming that the difference between the PA and nitric oxide affinity for alcohols, ~144 kcal, is the same as that for carbonyl compounds.

Table IV. Estimated Enthalpy Changes for Ion Molecule Reactions of the Nitrosonium Ion with Alcohols

reactant	product	ΔH, kcal/mol	reactant	product	ΔH, kcal/mol
Electrophilic Addition (Eq 1)			Hydroxide Abstraction (Eq 4 or 5)		
CH_3OH	CH_3OHNO^+	−31	CH_3OH	CH_3^+	+51.4
C_2H_5OH	$C_2H_5OHNO^+$	−34	C_2H_5OH	$CH_3CH_2^+$	+16.4
n-C_3H_7OH	n-$C_3H_7OHNO^+$	−33.5	n-C_3H_7OH	$C_2H_5CH_2^+$	+9.9
n-C_4H_9OH	n-$C_4H_9OHNO^+$	−36.4	n-C_4H_9OH	n-$C_3H_7CH_2^+$	+7.0
i-C_3H_7OH	i-$C_3H_7OHNO^+$	−36	sec-C_4H_9OH	$C_2H_5CHCH_3^+$	−7.8
t-C_4H_9OH	t-$C_4H_9OHNO^+$	−33	t-C_4H_9OH	$(CH_3)_3C^+$	−13.6
Hydride Abstraction (Eq 2 or 3)			Oxidation Plus Electrophilic Addition (Eq 13)		
CH_3OH	CH_2OH^+	+3.4	CH_3OH	CH_2ONO^+	−1.9
C_2H_5OH	CH_3CHOH^+	−10.7	C_2H_5OH	CH_3CHONO^+	−16.3
n-C_3H_7OH	$C_2H_5CHOH^+$	−14.5	n-C_3H_7OH	$C_2H_5CHONO^+$	−19.8
n-C_4H_9OH	n-$C_3H_7CHOH^+$	−15.1	i-C_3H_7OH	$(CH_3)_2CONO^+$	−28.2
i-C_3H_7OH	$(CH_3)_2COH^+$	−22.9			

on attachment of NO^+ is less than that for donation of a proton from CH_5^+, we anticipate that ions characteristic of sample molecular weight will be more abundant in nitric oxide rather than in methane chemical ionization mass spectra. Data obtained on alkanes (*7*), olefins (*8*), alcohols, aldehydes, ketones, esters, and carboxylic acids (*6*) confirm this expectation.

As shown in Table I, the most abundant ion in the nitric oxide chemical ionization mass spectrum of methanol corresponds to $(M + NO)^+$. Formation of $(CH_3ONO + NO)^+$ also occurs but the reaction pathway leading to this product ion has not been investigated. $(M + NO)^+$ ions appear in the spectra of higher molecular weight alcohols, but their abundance decreases with increasing ion source temperature. Fragmentation of the $(M + NO)^+$ adduct ion by the exothermic channels discussed below competes successfully with collisional stabilization for the longer chain alcohols.

Hydride Abstraction. Abstraction of hydride from the α-carbon of primary and secondary alcohols affords protonated aldehydes and ketones, respectively (eq 2 and 3). As shown

$$RCH_2OH + NO^+ \rightarrow RCHOH^+ + HNO \qquad (2)$$

$$R_2CHOH + NO^+ \rightarrow R_2COH^+ + HNO \qquad (3)$$

in Table IV this reaction is exothermic for all primary and secondary alcohols except methanol and accounts for 12–49% of the total sample ion current in the nitric oxide chemical ionization mass spectra of these compounds (Table I). Hydride abstraction is not an important reaction for methanol in agreement with the calculated enthalpy change of +3.4 kcal for this process (Table IV). Previously we reported that hydride abstraction from alkanes by NO^+ is nearly a thermoneutral reaction (*7*). The lower change in enthalpy associated with attack of NO^+ on the hydrocarbon chain relative to that calculated for reaction at the α-carbon, the favorable energetics for electrophilic addition of NO^+ at oxygen, and the known dependence of ion molecule reaction rates on the polarizability and dipole moment of the neutral substrate (*15*) all suggest that hydride abstraction should occur preferentially by formation of **42** followed by a 1,2-elimination of HNO. In agreement with this proposal we find that the α-deuterium labeled alcohols in Table II lose DNO exclusively under nitric oxide chemical ionization conditions and form $(M - 2)^+$ ions rather than $(M - 1)^+$ ions.

Hydroxide Abstraction. As shown in Table IV, electrophilic addition of NO^+ at oxygen to give **42** followed by elimination of nitrous acid and formation of a carbonium ion (eq 4 and 5) is exothermic for secondary and tertiary alcohols but endothermic for most primary alcohols. Accordingly, we expect nitric oxide chemical ionization mass spectra of secondary and tertiary, but not primary alcohols, to exhibit abundant $(M - OH)^+$ ions. The results displayed in Table I are in agreement with this expectation.

$$R_2CHOH + NO^+ \rightarrow R_2CH^+ + HONO \qquad (4)$$

$$R_3COH + NO^+ \rightarrow R_3C^+ + HONO \qquad (5)$$

Oxidation Plus Electrophilic Attachment of NO^+. Formation of $(M - 2 + NO)^+$ ions in the nitric oxide chemical ionization mass spectra of primary and secondary, but not tertiary, alcohols can be pictured formally as involving oxidation of the alcohol and subsequent attachment of NO^+ to the resulting aldehyde or ketone. Evidence that neutral nitric oxide is involved in this reaction was obtained by recording spectra of butanol and decanol using a dilute mixture of nitric oxide in nitrogen ($N_2/NO = 20/1$) as the chemical ionization reagent gas. In this mixture NO^+ is produced by charge exchange with N_2^+ (eq 6 and 7) and is still the dominant

$$N_2 + e^- \rightarrow N_2^+ + 2e^- \qquad (6)$$

$$N_2^+ + NO \rightarrow N_2 + NO^+ \qquad (7)$$

reagent ion but the probability of sample ions colliding with neutral nitric oxide molecules is greatly reduced. Under these conditions both the $(M - 2 + NO)^+$ and the $(M - 3)^+$ ions disappear completely from the nitric oxide spectra of butanol and decanol. This result is consistent with the findings of Williamson and Beauchamp (*9*) who failed to observe these two ion types when nitric oxide was allowed to react with primary alcohols under the low-pressure operating conditions of the ion cyclotron resonance technique. Experiments with methanol-d_4 and 1,1-deuterated primary alcohols (Table II) indicate that it is the hydrogens bonded to oxygen and the α-carbon of the alcohol that are lost in the formation of the $(M - 2 + NO)^+$ ion.

Initially it was suspected that this oxidation reaction might involve stepwise abstraction of hydrogen radicals from carbon and oxygen by neutral nitric oxide followed by attachment of NO^+ to the resulting aldehyde as shown in eq 8–10. The

$$CH_3CH_2OH + NO \rightarrow CH_3CH_2O\cdot + HNO \qquad \Delta H = +61 \text{ kcal} \quad (8)$$

$$CH_3CH_2O\cdot + NO \rightarrow CH_3CHO + HNO \qquad (9)$$

$$CH_3CHO + NO^+ \rightarrow CH_3CHONO^+ \qquad (10)$$

first step in this process, however, is estimated to be highly endothermic and therefore unlikely under our experimental conditions. The nonexistence of this pathway was confirmed by taking methane chemical ionization mass spectra of aliquots over a 2-h period from a mixture of heptanol and nitric oxide at 1 torr in a glass bulb heated at 250 °C. Only starting alcohol was detected in these experiments. An oxidation pathway initiated by nitric oxide is also difficult to reconcile with the absence of $(M - 2 + NO)^+$ ions in the nitric oxide chemical ionization mass spectrum of 2-phenylethan-1-ol, **17**, and the finding that only one of two hydroxyl groups is oxidized in the diol, **41**.

A second mechanism for formation of $(M - 2 + NO)^+$ ions involving transfer of hydride and a hydrogen radical to the nitrosonium ion followed by attachment of nitric oxide to the resulting aldehyde radical cation also seems unlikely due to the high endothermicity associated with the first step in this pathway (eq 11 and 12).

$$CH_3CH_2OH + NO^+ \rightarrow CH_3CHO^{+\cdot} + HONH\cdot \qquad \Delta H = +44 \text{ kcal} \quad (11)$$

$$CH_3CHO^{+\cdot} + NO \rightarrow CH_3CHONO^+ \qquad (12)$$

To explain the experimental results we suggest that formation of $(M - 2 + NO)^+$ ions involves electrophilic addition of NO^+ to the oxygen of the alcohol followed by collision with, and transfer of two hydrogens to, a molecule of nitric oxide.

$$CH_3CH_2OH + NO^+ + NO \rightarrow CH_3CHONO^+ + HONH\cdot \qquad (13)$$

As shown in Table IV, this process is exothermic for all primary and secondary alcohols. Since this mechanism requires a multistep process and therefore a long-lived ion molecule complex containing one molecule of alcohol and one molecule of NO^+, the abundance of the $(M - 2 + NO)^+$ ions should be strongly dependent on ion source temperature. Increasing the internal energy of the neutral reactants should increase the vibrational energy of the bimolecular ion molecule complex, shorten its lifetime, and reduce the probability that it will form a long-lived complex with another molecule of nitric oxide. A corresponding increase in the abundance of product ions derived from unimolecular decomposition of the initial bimolecular adduct ion **42** would be expected. Consistent with this interpretation is the finding that the abundance of the $(M - 1)^+$ for **12** nearly doubles when the ion source temperature increases from 100 to 230 °C (Table I).

$(M - 3)^+$ Ion Formation. The occurence of appropriate metastable ions in the nitric oxide chemical ionization mass spectra of primary alcohols indicates that all or part of the $(M - 3)^+$ ions result from elimination of HNO from $(M - 2 + NO)^+$ ions. As shown in Table II, loss of HNO competes with loss of DNO in the spectra of 1,1-deuterated primary alcohols. This result suggests that more than one cyclic transition state must be involved in the elimination step.

$$RCHONO^+ \rightarrow RCO^+ + HNO \qquad (14)$$

A similar situation prevails in the formation of $(M - 1)^+$ ions in the nitric oxide chemical ionization mass spectra of aldehydes. We assume that this reaction proceeds through initial formation of an adduct between NO^+ and the aldehyde having a structure identical with that of the $(M - 2 + NO)^+$ ion derived from the corresponding alcohol. In the spectrum of heptanal-*1-d* ions resulting from

$$CH_3CHO + NO^+ \rightarrow CH_3CHONO^+ \rightarrow RCO^+ + HNO \qquad (15)$$

$$\Delta H = -17 \text{ kcal}$$

loss of hydride and deuteride carry 5% and 80% of the total ion current, respectively. $(M + NO)^+$ ions account for the remainder of the sample ion current.

Analytical Considerations. Unlike 70-eV electron ionization (*1*) and methane (*2*) or isobutane (*3*) chemical ionization mass spectra of alcohols, nitric oxide spectra of this class of compounds exhibit abundant ions characteristic of sample molecular weight. In addition, primary, secondary, and tertiary alcohols undergo different sets of ion molecule reactions with NO^+ and therefore can be differentiated by nitric oxide chemical ionization mass spectrometry. Multifunctional organic compounds have not been studied as yet but the results obtained on the aromatic alcohol **17** suggest that the above conclusion will only be valid when the alcohol group is the preferred site of reaction in the sample. In the case of **17**, products of charge exchange and electrophilic addition to the aromatic ring dominate the nitric oxide chemical ionization spectrum (eq 16 and 17). The total

$$C_6H_5CH_2CH_2OH + NO^+ \rightarrow HOCH_2CH_2C_6H_5^{+\cdot} + NO \qquad (16)$$

$$C_6H_5CH_2CH_2OH + NO^+ \rightarrow HOCH_2CH_2C_6H_5NO^+ \qquad (17)$$

sample ion current generated under chemical ionization conditions with either methane or nitric oxide as reagent gases is about the same.

496 Anal. Chem. 1982, 54, 496-499

ACKNOWLEDGMENT

The authors thank J. Futrell, Department of Chemistry, University of Utah, for the sample of **38**, J. A. McCloskey, Department of Biopharmaceutical Science, University of Utah, for samples **40** and **41**, and C. Fenselau, Department of Pharmacological and Experimental Therapeutics, Johns Hopkins University, for the sample of heptanal-*1-d*. We also acknowledge the assistance of C. Devine in the preparation of several deuterium-labeled alcohols.

LITERATURE CITED

(1) Budzikiewicz, A. H.; Djerassi, C.; Williams, D. H. "Mass Spectrometry of Organic Compounds"; Holden-Day: San Francisco, CA, 1967; pp 94-124.

(2) Munson, M. S. B.; Field, F. H. *J. Am. Chem. Soc.* **1966**, *88*, 2621-2630.

(3) Field, F. H. *J. Am. Chem. Soc.* **1970**, *92*, 2672-2676.

(4) Einolf, N.; Munson, B. *Int. J. Mass Spectrom. Ion Phys.* **1972**, *9*, 141-160.

(5) Jelus, B.; Munson, B.; Fenselau, C. *Anal. Chem.* **1974**, *46*, 729-730.

(6) Hunt, D. F.; Ryan, J. F. *J. Chem. Soc., Chem. Commun.* **1972**, 620-621.

(7) Hunt, D. F.; Harvey, T. M. *Anal. Chem.* **1975**, *47*, 1965-1969.

(8) Hunt, D. F.; Harvey, T. M. *Anal. Chem.* **1975**, *47*, 2136-2141.

(9) Williamson, A. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5714-5718.

(10) Meot-Ner, M.; Field, F. H. *J. Am. Chem. Soc.* **1975**, *97*, 2014-2017.

(11) Honma, K.; Tanaka, K.; Koyano, I.; Tanaka, I. *J. Chem. Phys.* **1976**, *65*, 678-683.

(12) Beggs, D.; Vestal, M. L.; Fales, H. M.; Milne, G. W. A. *Rev. Sci. Instrum.* **1971**, *42*, 1578-1584.

(13) Hunt, D. F.; McEwen, C. N.; Harvey, T. M. *Anal. Chem.* **1975**, *47*, 1730-1734.

(14) Hunt, D. F.; Stafford, G. C.; Crow, F. W.; Russell, J. W. *Anal. Chem.* **1976**, *48*, 2098-2105.

(15) Su, T.; Bowers, M. T. *J. Am. Chem. Soc.* **1973**, *95*, 7609-7610.

RECEIVED for review July 10, 1981. Accepted October 29, 1981. This research was supported by grants from the U.S. Army Research Office, DAAG 29-76-G-0326, and the National Science Foundation.

Determination of Cadmium in Lake Michigan by Mass Spectrometric Isotope Dilution Analysis or Atomic Absorption Spectrometry Following Electrodeposition

Jean Muhlbaier, Charles Stevens, Donald Graczyk, and Thomas Tisue*

Ecological Sciences Section, Radiological and Environmental Research Division, Argonne National Laboratory, Argonne, Illinois 60439

Electrodeposition on an amalgamated gold wire concentrates cadmium effectively from freshwater for subsequent determination by mass spectrometric isotope dilution analysis or by electrothermal atomic absorption spectrometry. Sampling and handling procedures have been developed that reduce blanks to $\sim$3 ng L^{-1} while avoiding the need for clean room operations. By use of mass spectrometric isotope dilution, the calculated instrumental limit of detection was $<$0.1 ng, well below the limits imposed by the observed precision and blank values. The overall procedure, including determination of and correction for the blank value, had a precision of 14%, relative standard deviation. Electrothermal atomic absorption spectrometric detection gave a relative precision of 19%. The mean cadmium concentration in Lake Michigan water samples from 1978 ranged from 31 to 41 ng L^{-1}.

Reliable determination of ultratrace amounts of heavy metals in natural waters has provided many challenges to analysts. Contamination problems often become severe at levels below 100 ng L^{-1}. Special sampling and handling methods are obligatory, and clean room conditions may be required (*1*, *2*). Ultra-high-purity reagents and special containers add to cost and inconvenience. Samples often may require extensive chemical and physical treatment to remove interfering species, and even then, preconcentration is frequently necessary to bring amounts within the range of detectability. These isolation and enrichment steps add to the risk of contamination and can lead to low recovery.

Several analysts have recognized that electrodeposition (ED) offers unique advantages in overcoming these myriad difficulties. The procedure is selective for metals reducible in aqueous solution and therefore lessens potential interferences from elements in groups 1A, 2A, and 7A of the periodic table. Because little or no chemical modification of the sample is usually necessary, the risk of contamination from impure reagents diminishes. Incorporating the working electrode directly into the sample container eliminates contamination due to transfer and handling.

Batley and Matousek (*3*) and Torsi (*4*), following earlier reports by Brandenberger and Bader (*5*) and Fairless and Bard (*6*), electrodeposited several metals from seawater directly onto graphite furnace tubes for determination by atomic absorption spectrometry (AAS). Fairless and Bard (*7*) also demonstrated the advantages of electrodeposition onto a mercury drop, which they subsequently transferred to a graphite furnace for analysis by AAS. Cadmium has been concentrated from seawater by electrodeposition onto a platinum filament (*8*). The filament was heated electrically in the optical path of an AAS instrument for analysis.

As attractive as these procedures seem, none answers the objection that recovery from real samples may not be quantitative, especially at very low levels. An independent means of determining yield is lacking. Catanzaro (*9*) coupled electrodeposition onto platinum with mass spectrometric isotope dilution analysis (MSID) to determine Pb and Cu. The MSID technique is an appealing one for dealing with ultratrace metal analyses because of its high sensitivity and specificity. But its greatest advantage is that it makes quantitative recovery unnecessary, once isotopic equilibration is assured. On the other hand, MSID analysis is rather time-consuming and requires costly equipment operated by highly skilled personnel. The cost per analysis is high. Earlier determinations of Cd in natural waters by MSID relied on separation schemes carried out in clean rooms (*2*). As a result, MSID analysis is best viewed as a reference method against which other simpler and less costly procedures may be evaluated. Accordingly, we used MSID to assess the efficiency of the electrodeposition and stripping procedure described here and to study control of contamination in sampling and handling operations. Our results suggest that caution be used in interpreting the results

0003-2700/82/0354-0496$01.25/0