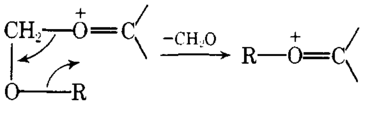
Internal Solvation, Entropy, and Energy Effects on Alternative Channels for a Single Reaction. Methoxyl vs. Methyl Migration in the (M − methyl)$^+$ Ion from Methoxymethyl Isopropyl Ether

Sir:

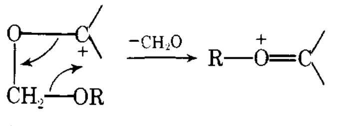
It is well known that the rate constants, $k(\epsilon)$, for competitive unimolecular reactions of an isolated species may cross, so that the dominant process at low energy becomes the minor process at high energy. In mass spectrometry, interest in this situation has focused upon the relative abundances of ions formed in the source (high internal energy reactants) vs. those formed from the lower energy metastable ions. The reactions leading to abundant metastable peaks typically have low activation energies as well as low frequency factors while the competitive processes which dominate in the ion source have higher activation energies and higher frequency factors.[1] This simple concept has found wide usefulness in mass spectrometry.[2]

We now show that such a cross-over in $k(\epsilon)$ curves can occur for competitive reactions from the *same* reactant which lead to the *same* products. The reaction channel followed depends upon the internal energy of the reactant, and the results show the relative importances of the channels to vary by a factor of 10^3 in the accessible energy range. A decade ago,[3] alkyl migration was proposed in the loss of formaldehyde from ions generated via α-cleavage from acetals.



(1)

The expulsion of formaldehyde might, however, occur via alkoxyl migration to a carbenium center a well-known reaction type in gaseous ion chemistry.[4]



(2)

Methoxymethyl isopropyl ether has been selected as a model compound to differentiate between mechanisms 1 and 2 which would both lead to precisely the same products distinguishable only by isotopic labeling. Its 70-eV mass spectrum[5] exhibits, in addition to the base peak at *m/e* 45 ($CH_3OCH_2^+$), peaks at *m/e* 89 and *m/e* 59, which are relevant to the present study. These are due to the following fragmentations of the molecular ion.

$$\underset{<0.1\%}{M^+ = 104} \xrightarrow{-CH_3} \underset{34.0\%}{m/e\ 89} \xrightarrow{-CH_2O} \underset{7.1\%}{m/e\ 59} \qquad (3)$$

Upon simultaneous replacement of all isopropyl hydrogen atoms by deuterium and ^{18}O substitution of the methoxy oxygen atom,[6] the peaks *m/e* 45 and *m/e* 89 shift completely to *m/e* 47 ($CH_3{}^{18}OCH_2^+$) and *m/e* 95 = $(M - CD_3)^+$ when correction is made for the incomplete ^{18}O labeling.[6] The peak *m/e* 59, however, shifted approximately 90% to *m/e* 65 and 10% to *m/e* 63, as calculated from relative intensities corrected for the incomplete ^{18}O labeling.

$$\underset{<0.1\%}{M^+ = 113} \xrightarrow{-CD_3} \underset{37.7\%}{m/e\ 95} \begin{cases} \xrightarrow{-CH_2{}^{18}O} \underset{6.9\%}{m/e\ 65} \\ \xrightarrow{-CH_2{}^{16}O} \underset{0.9\%}{m/e\ 63} \end{cases} \qquad (4)$$

High-resolution mass measurements[13] confirmed that *m/e* 65 contains the ^{18}O atom and *m/e* 63 the ^{16}O atom. Furthermore, the hydrogen atoms of the expelled formaldehyde molecule originate exclusively from the original methylene group, as evidenced by the mass spectrum and exact mass measurements on the trideuteriomethoxymethyl isopropyl ether[14] which shows full retention of all deuterium atoms both in the (M − methyl)$^+$ and in the (M − methyl − formaldehyde)$^+$ ions.

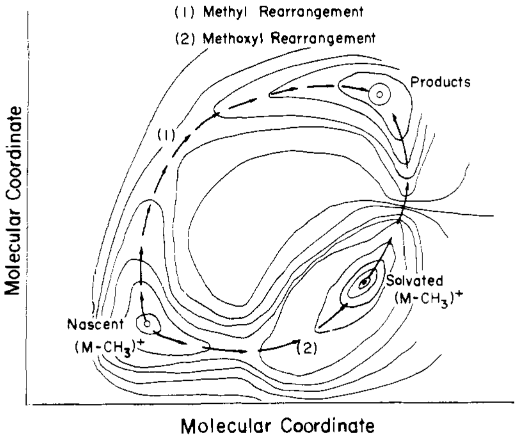


Figure 1. Potential energy contour diagram illustrating alternative paths (reactions 1 and 2 in text) from reactant to product. In methoxyl rearrangement (2) the system passes through or close to the stable solvated reactant ion which is accessible via a low barrier. The transition state energy if this pathway is chosen is higher than that for the alternative methyl rearrangement pathway.

All data are, therefore, consistent with the expulsion of formaldehyde from the (M − methyl)$^+$ ion via approximately 90% methoxyl migration (mechanism 2) vs. 10% methyl migration (mechanism 1) at 70 eV in the ion source; the same is true at 15 eV but upon further lowering the electron energy the percentage of methyl migration gradually increases up to 40% at 11 eV. In striking contrast, metastable (M − methyl)$^+$ ions fragment virtually exclusively by methyl migration (1). Methoxyl migration is just detectable (<1%) in the reversed geometry MIKE spectrometer.[15] Ions of intermediate energy[17] were studied by collision-induced dissociation[18] in the MIKE spectrometer. As expected, these ions showed intermediate behavior with methyl migration accounting for 90% of the total and methoxyl the remaining 10%.

The reaction studied is unusual[19] in that two routes from the same reactants to the same products are involved. Both reactions involve four-centered rearrangements, making their contrasting $k(\epsilon)$ behavior the more notable. The experimental data require that methoxyl migration has the higher activation energy and the higher frequency factor. A higher activation energy is reasonable since one of the two C-O bonds cleaved has considerable double bond character in this, but not in the methyl migration, mechanism. We suggest that the higher frequency factor for methoxyl migration is a consequence of internal solvation of charge in the (M − methyl)$^+$ ion by the nucleophilic methoxyl group.[20] This will tend to lock the ion into a configuration favorable to this rearrangement. The situation is summarized in Figure 1.

These results show the considerable power of the combination of isotope labeling and kinetic energy release measurements. The existence of competitive reaction channels from the same reactant to the same products through intermediates of the same ring size which have quite distinct kinetic behavior, as influenced in particular by internal solvation of ions, is the major finding of this work.

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MS902 mass spectrometer. Support of the Purdue effort by the National Science Foundation is gratefully acknowledged.

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(5) Low resolution mass spectra were obtained at 70 eV on an AEI MS902 instrument with sample introduction via the heated inlet system.

(6) 1,1,1,2,3,3,3-Heptadeuteropropanol-2, obtained by reduction of hexadeuterioacetone with $LiAlD_4$,[7,8] was treated with formaldehyde and hydrogen chloride to give chloromethyl heptadeuterioisopropyl ether.[9,10] Reaction of the latter compound with $CH_3{}^{18}OH$, prepared from $H_2{}^{18}O$ and $HC(OCH_2CH_2CH_2CH_3)_3$ as described in the literature,[11] in pyridine gave $CH_3{}^{18}OCH_2{}^{16}OCD(CD_3)_2$[12] which was purified by GLC using successively OV-1 and QF-1 columns, operated at 60°. From measurements with the AEI MS902 instrument at 15 eV it was found to contain 98.2% d_7, 1.8% d_6, 53.8% ^{18}O, and 46.2% ^{16}O.

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(13) AEI MS902 at 12,000 resolution (10% valley).

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(15) The mass-analyzed ion kinetic energy spectrometer[16] was operated at 7.4 kV accelerating voltage, 100 μA trap current, 6×10^{-6} Torr indicated source pressure, 2×10^{-7} analyzer pressure, and 0.030-in. final slit.

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A Facile Diazenium Cation–Hydrazyl Radical–Nitroxide Radical Equilibrium. The Significance of Charge-Transfer Intermediates

Sir:

The dynamics of the diazenium cation–hydrazyl radical equilibrium and associated redox and proton-transfer equilibria have been the subject of intense investigation recently.[1,2] The studies have succeeded largely as a consequence of the successful preparation of a series of stable trialkyl diazenium salts.[2] In the present report, we disclose a new synthetic entry to this compound class, the occurrence of easily detected charge-transfer complexes, and the significance of C-T interactions for the diazenium cation–hydrazyl radical equilibrium. In addition, the generation of the first 1,2-dialkyl-2-arylhydrazyl radical, a species in equilibrium with a cyclic nitroxide radical, is described.

Table I. Ultraviolet and Visible Absorption Maxima as a Function of Solvent for the *tert*-Butyldiazenium Salts 2^+ and the 2,4-Dinitrophenyldiazenium Bromide 4^+ (λ_{max}, nm ($\epsilon_{apparent}$, M^{-1} cm^{-1})[a,b]

	H_2O	CH_3OH	CH_3CN	CH_2Cl_2
$2^+ClO_4^-$	311 (99)	311 (96)	311 (100)	312 (100)
2^+Cl^-–3	310 (100)	311 (110)	310 (100)	300 (195)[c]
2^+Br^-–3	310 (99)	311 (100)	310 (130) 350 (25) sh	308 (220) 346 (160) sh
2^+I^-–3	310 (110) 350–600 (<10)[d]	311 (120) 360 (30) sh	311 (120) 404 (30)	310 (190) 436 (380)
$4^+ClO_4^-$	284 (6500)	285 (6400) sh	286 (7400)	291 (6000)
4^+Br^-–7	280 (6700) sh	285 (6200) sh	285 (6600) 425 (105)[e] sh	288 (6900) 458 (370)[f]

[a] Calculated from the observed optical density and the initial concentration. Except were noted, the latter was 1.0×10^{-2} M for all 2^+ salts and 1.0×10^{-4} M for 4^+X^-. [b] All of the substances listed likewise show high intensity absorption <230 nm. [c] This band is significantly broader than the corresponding peak for $2^+ClO_4^-$. [d] A long tail with no distinct λ_{max}. [e] 1.0×10^{-2} M. [f] 1.0×10^{-3} M.

Treatment of 2,3-diazabicyclo [2.2.2]oct-2-ene (DBO)[3] with 1 equiv of $HClO_4$ (Et_2O, 25°) leads to the stable protio-diazenium cation $\mathbf{1}^+ClO_4^-$ (mp 210-212°, 87%).[4] The latter is smoothly converted to the *tert*-butyl salt $\mathbf{2}^+ClO_4^-$ (mp 242-243°, 90%) upon refluxing in *tert*-butyl alcohol.[5] Alternative counterions are obtained by ion exchange ($\mathbf{2}^+$, Bio-Rad AG MP-1: Cl^-, mp 191-192°, 79%; Br^-, mp 226-227°, 88%; NaI-CH_2Cl_2: I^-, mp 223-224°, 91%).

Table I displays the uv-visible absorption maxima for the series $\mathbf{2}^+$. In strongly ionizing solvents (H_2O, CH_3OH), each salt exhibits a weak band at 310 nm (ϵ 100-120 M^{-1} cm^{-1}) attributed to the diazenium moiety. As the solvent polarity is reduced, an additional band which does not obey Beer's law appears at longer wavelengths. The magnitude of the effect descends in the following order, X: I > Br > Cl. The influence of the solvent on the uv-visible spectra, the relative ionization potentials of the gegenions,[6] and the position of the new absorption maxima permit assignment of the latter to the long-wavelength charge-transfer band[7-9] of complex **3**.

Suitable modification of the heterocyclic acceptor moiety which leads to a decrease in the energy of the lowest unoccupied molecular orbital,[7c,9] can be expected to lead to a magnification of the acceptor properties of $\mathbf{2}^+$. Charge transfer might then proceed to complete electron transfer. Accordingly, treatment of DBO with 2,4-dinitrobromobenzene (Et_2O, 25°) occurs cleanly to give the phenylated system $\mathbf{4}^+Br^-$ (mp 152-153°, 83%). Exchange of the bromide ion ($NaClO_4$-H_2O) furnishes $\mathbf{4}^+ClO_4^-$ (mp 179-180°). Analogous to the *tert*-butyl salts $\mathbf{2}^+$, compound $\mathbf{4}^+Br^-$ exhibits charge-transfer behavior in the uv-visible with broad low energy absorption at 458 nm in CH_2Cl_2, whereas the perchlorate salt is transparent in this region (Table I). Halide exchange (NaI-H_2O) yields $\mathbf{4}^+I^-$ (mp 119-120°, 73%) a purple diamagnetic solid (Gouy balance determination). On the contrary, dissolution of the latter in CH_2Cl_2, halide exchange of $\mathbf{4}^+Br^-$ in organic media (NaI-CH_2Cl_2), or direct alkylation of DBO with 2,4-dinitroiodobenzene (Et_2O or C_6H_6, reflux) yields a green paramagnetic solution (λ_{max}(CH_2Cl_2) 690 nm (ϵ 6500 M^{-1} cm^{-1})) with an ESR spectrum of three lines of equal intensity ($g = 2.0038$, $a_N = 12.2$ G, C_6H_6). Further resolution into about 40 lines could be achieved by degassing, but the hyperfine couplings were not assigned. The solution is stable to oxygen for 9-12 hr. No other radical is evident after the original ESR signal disappears, in contrast to observations for trialkyl hydrazyl radicals.[2b] The same paramagnetic species is generated by