Chromic Acid Oxidation of 1-*p*-Tolyl-2-phenylethanol in the Presence of Acrylamide or Acrylonitrile. To 50 ml of the normal reaction mixture was added 5 g of acrylamide or acrylonitrile. After the oxidation, the reaction mixture was worked up and analyzed by nmr as described for the competition studies.

Radical Trapping Experiments with Oxygen. A chromic acid oxidation of 1,2-diphenylethanol was carried out in the normal fashion except that oxygen was bubbled through the reaction mixture during the oxidation. In a control experiment, nitrogen was bubbled through the solution instead of oxygen. In another experiment, benzyl alcohol was added to a prereduced chromium solution, and oxygen was bubbled through the solution while it was heated for the same amount of time needed to oxidize the 1,2-diphenylethanol. All of these runs were worked up and analyzed as described for the competition runs.

1-*p*-Tolyl-2-phenylethanol was oxidized by chromic acid in 93% acetic acid being 1 *M* in sodium acetate, with oxygen bubbling through the reaction mixture in one run and nitrogen bubbling through the reaction mixture in another run. These runs were worked up and analyzed as described for the competition runs except that no standard was added.

Products of the Chromic Acid Oxidation of 1,2-Diphenylethanol as a Function of Time. To 12.5 ml of 85% acetic acid, 0.5 *M* in sodium acetate, was added 4 mmol of 1,2-diphenylethanol. In another flask 4 mmol of chromium trioxide was dissolved in 12.5 ml of the solvent. Both solutions were heated to 77°, flushed with nitrogen, combined, and kept at 77° under nitrogen. Aliquots of 5 ml were taken after 1, 5, and 10 min and were added to 10 ml of a cooled saturated NaCl solution. The standard was added with 10 ml of ether and the mixtures were worked up and analyzed as described for the competition runs.

Products of the Chromic Acid Oxidation of 1,2-Diphenylethanol in the Presence of Added Chromium(III). 1,2-Diphenylethanol (1.6 mmol) was dissolved in 7.5 ml of the prereduced chromium solution and 1.2 mmol of chromium trioxide was added. After the reaction mixture was heated for 20 min, 7.5 ml of 85% acetic acid, 0.5 *M* in sodium acetate, was added along with 0.565 g of the standard, and the mixture was worked up and analyzed as described for the competition runs. In the control experiment, the alcohol and chromium trioxide were dissolved in 7.5 ml of 85% acetic acid, 0.5 *M* in sodium acetate. After heating, 7.5 ml of the prereduced chromium solution and 0.565 g of the standard were added and the mixture was worked up and analyzed.

Positive and Negative Ion–Molecule Reactions and the Proton Affinity of Ethyl Nitrate

Peter Kriemler[1a] **and S. E. Buttrill, Jr.**[1b]

Contribution from Varian Associates, Analytical Instrument Division,
Palo Alto, California 94303, and the Department of Chemistry,
Stanford University, Stanford, California 94305. *Received September 9, 1969*

Abstract: Ion cyclotron single and double resonance techniques have been used to study the positive and negative ion–molecule chemistry of ethyl nitrate. The positive ion–molecule reactions can be divided into three classes: (1) transfer of NO_2^+ from $CH_2ONO_2^+$ and $H_2NO_3^+$ to ethyl nitrate to form $C_2H_5N_2O_5^+$; (2) protonation of ethyl nitrate by $C_2H_3^+$, $C_2H_5^+$, and CHO^+; and (3) fragmentation of protonated ethyl nitrate into $H_2NO_3^+$ and ethylene. Proton transfer reactions were used to determine that $\Delta H_f(C_2H_5ONO_2H^+) = 149 \pm 3$ kcal/mol, corresponding to a value of 180 ± 3 kcal/mol for the proton affinity of ethyl nitrate. The only negative ion–molecule reactions in pure ethyl nitrate are the reactions of $C_2H_3O^-$, $C_2H_5O^-$, and OH^- to produce NO_3^-. Mixtures of ethyl nitrate with methanol, ethanol, 2-propanol, acetone, propionaldehyde, and *n*-propyl chloride showed that most of the negative ion reactions were proton transfers, although several displacement-like reactions were also found. The NO_2^- ion was completely unreactive. A value of $\Delta H_f(CH_3O^-) = -30 \pm 6$ kcal/mol is deduced from the observed proton transfer reactions. The large cross section at zero electron energy for the formation of NO_2^- by dissociative resonance capture makes ethyl nitrate an excellent detector for near-zero energy electrons. An electron impact excitation spectrum of carbon disulfide was obtained using the NO_2^- peak from ethyl nitrate to monitor the number of inelastically scattered electrons as a function of electron energy.

Although the positive[2,3] and negative[4] ion mass spectra of ethyl nitrate have been studied in some detail, no study of the gas phase ion–molecule chemistry of this or any other nitrate has been reported. In view of the richness of the ion–molecule chemistry of the nitroalkanes,[5] ion cyclotron resonance (ICR) spectrometry has been used to study the positive and negative ion–molecule reactions in ethyl nitrate.

An ICR spectrometer[6,7] is capable of operating at pressures and ion residence times such that extensive ion–molecule reactions can occur. Ion detection and mass resolution are based on the fact that an ion of mass *m* in a uniform magnetic field *H* moves in a circular orbit with angular frequency

$$\omega_c = qH/mc$$

where *q* is the ion charge and *c* is the speed of light. If an rf electric field $E_1(t)$ is applied perpendicular to *H* at the cyclotron frequency ω_c of one of the ionic species present, then those ions will absorb energy from the electric field and be accelerated to larger cyclotron orbits and kinetic energies. Sweeping the magnetic field while recording the power absorbed from a fixed-frequency marginal oscillator detector produces a mass spectrum of the ions in the spectrometer. In addition to this single resonance experiment, a double resonance technique is also available which

---

[1] (a) Varian Postdoctoral Fellow, 1968–1969; (b) address correspondence to this author at the Chemistry Department, University of Minnesota, Minneapolis, Minn. 55455.

[2] J. E. Collin, *Bull. Soc. Roy. Sci. Liege*, **32**, 133 (1963).

[3] R. T. M. Fraser and N. C. Paul, *J. Chem. Soc.*, *B*, 659 (1968).

[4] K. Jäger and A. Henglein, *Z. Naturforsch.*, *A*, 22, 700 (1967).

[5] P. Kriemler, submitted for publication.

[6] J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

[7] J. M. S. Henis, *J. Amer. Chem. Soc.*, **90**, 844 (1968).

Table I. ICR Spectra of Ethyl Nitrate at Low and High Pressure at 30 eV

m/e	Species	Relative intensities 10^{-7} Torr	Relative intensities 10^{-5} Torr
15	CH_3^+	1.0	1.0
26	$C_2H_2^+$	~0.5	~0.5
27	$C_2H_3^+$	3.7	1.0
28	$C_2H_4^+$	2.7	2.8
29	$C_2H_5^+$, CHO^+	14, 14	14.0
30	CH_2O^+, (NO^+)	14.0	13.0
31	NOH^+	2.7	5.8
43	$C_2H_3O^+$	7.0	5.8
44	$C_2H_4O^+$	1.0	1.2
45	$C_2H_5O^+$	1.5	2.0
46	NO_2^+	100.0	100.0
64	$H_2NO_3^+$		5.5
76	$CH_2ONO_2^+$	55.0	31.5
90	$C_2H_4ONO_2^+$		1.7
91	$CH_3CH_2ONO_2^+$		
92	$CH_3CH_2ONO_2H^+$		19.5
137	$CH_3CH_2ONO_2NO_2^+$		31.8

Table II. Positive Ion-Molecule Reactions in Ethyl Nitrate

Reaction	dk/dE_{ion}	ΔH, kcal/mol
(1) $CH_2ONO_2^+ + EtONO_2 \rightarrow EtONO_2NO_2^+ + CH_2O$	−	
(2) $H_2NO_3^+ + EtONO_2 \rightarrow EtONO_2NO_2^+ + H_2O$	−	
(3) $C_2H_5^+ + EtONO_2 \rightarrow EtONO_2H^+ + C_2H_4$	−	−20
(4) $CHO^+ + EtONO_2 \rightarrow EtONO_2H^+ + CO$	−	−61
(5) $C_2H_3^+ + EtONO_2 \rightarrow EtONO_2H^+ + C_2H_2$	−	−29
(6) $EtONO_2H^+ \rightarrow H_2NO_3^+ + C_2H_4$	+	(29)[a]

[a] Using a calculated (ref 10) value of ΔH_f ($H_2NO_3^+$) = 166 kcal/mol.

can determine which ions are reacting to form a particular ionic product. A double resonance experiment is performed by monitoring the concentration of a particular product ion and simultaneously applying a second rf electric field $E_2(t)$ at the cyclotron frequency of a possible reactant ion. The suspected reactant ion is translationally heated and this changes its reaction rate. If the observed and irradiated ions are chemically coupled, then a change will be observed in the signal from the observed ion. Sweeping the frequency of $E_2(t)$ over the cyclotron frequencies of all possible reactant ions produces a spectrum of the ions coupled by ion-molecule reactions to the observed ion. Using the single and double resonance experiments, it is possible to determine ion-molecule reaction sequences, even in complex systems.

Experimental Section

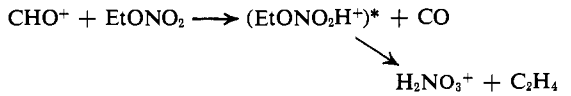
An unmodified Varian V-5900 ICR spectrometer was used for all of the experiments. All of the compounds were reagent grade and were purified by bulb-to-bulb distillation under vacuum. No impurities were detected in any of the low pressure single resonance spectra. An electron energy of 30 eV was used in most of the positive ion studies. The proton transfer reactions were also checked at 12.5 eV to minimize the possibility of producing vibrationally excited ions.

Results and Discussion

A. Positive Ions. Table I shows the relative ICR spectral intensities of the positive ions in pure ethyl nitrate at 10^{-7} and 10^{-5} Torr. The resolution of the ICR spectrometer was high enough to resolve the $C_2H_5^+$–CHO^+ doublet. Figure 1 shows a high resolution spectrum of the mass 29 region. The observing oscillator frequency was 691 kHz. The experimental mass difference of 0.0375 amu is in good agreement with the actual difference of 0.0364 amu.

The positive ion-molecule reactions identified with the double resonance technique are listed in Table II along with the sign of dk/dE_{ion}. A negative dk/dE_{ion} corresponds to a reaction rate constant which decreases with reactant ion energy and thus produces a negative double resonance signal.[8] A positive dk/dE_{ion} is indicated by a positive double resonance signal. It is important to note that a reaction which gives a negative double resonance signal *must* be occurring at thermal ion energies, but a reaction which gives a positive double resonance signal may or may not be occurring in the absence of the double resonance irradiation.

The dissociation of protonated ethyl nitrate to give the $H_2NO_3^+$ ion reaction 6 gave a positive double resonance signal. This signal could arise from a collision-induced fragmentation[9] of the translationally heated $EtONO_2H^+$ ion and reaction cannot be assumed to occur solely on the basis of the double resonance signal. In fact, negative double resonance signals from ions at *m/e* 27 and 29 are also found in the double resonance spectrum of $H_2NO_3^+$. These results suggest that the $H_2NO_3^+$ ion is formed by the fragmentation of excited protonated ethyl nitrate produced in reactions 3–5 (Table II). The amount of excitation required to produce this fragmentation can be estimated to be 29 kcal/mol using ΔH_f ($H_2NO_3^+$) = 166 kcal/mol. This value was obtained by Dewar, *et al.*,[10] from a semiempirical SCF MO calculation. Their method (MINDO) overestimated ΔH_f ($CH_3ONO_2^+$) by 23 kcal/mol, but underestimated ΔH_f ($EtONO_2H^+$) by 10 kcal/mol; the enthalpy change for reaction 6 of 29 kcal/mol shown in Table II is therefore only approximate. However, reaction 4 is certainly sufficiently exothermic to initiate the reaction sequence



$$\begin{tikzcd} CHO^+ + EtONO_2 \arrow[r] & (EtONO_2H^+)^* + CO \arrow[d] \\ & H_2NO_3^+ + C_2H_4 \end{tikzcd}$$

A similar sequence occurs beginning with reaction 5, but it may be entirely due to the presence of excited $C_2H_3^+$ ions.

B. Proton Affinity. The proton affinity (PA) of a molecule (M) is defined as minus the enthalpy change for the reaction $M + H^+ \rightarrow MH^+$. The hydrogen affinity (HA) can be similarly defined as minus the enthalpy change for the reaction $M^+ + H \rightarrow MH^+$.

---

[8] J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

[9] F. Kaplan, *J. Amer. Chem. Soc.*, **90**, 844 (1968).

[10] M. J. S. Dewar, M. Shanshal, and S. D. Worley, *ibid.*, **91**, 3590 (1969).

Table III. Proton Transfer Reactions Observed in Ethyl Nitrate Mixtures

$EtONO_2$ mixed with	Reactions observed	dk/dE_{ion}	Limit on PA ($EtONO_2$)
CH_3I	$CH_3IH^+ + EtONO_2 \rightarrow EtONO_2H^+ + CH_3I$	–	≥ 170
CH_3OH	$CH_3OH_2^+ + EtONO_2 \rightarrow EtONO_2H^+ + CH_3OH$	–	≥ 175
	$CH_3OH^+ + EtONO_2 \rightarrow EtONO_2H^+ + CH_3O$	–	≥ 168
	$CH_2OH^+ + EtONO_2 \rightarrow EtONO_2H^+ + CH_2O$	–	≥ 169
C_2H_5I	$EtIH^+ + EtONO_2 \rightarrow EtONO_2H^+ + EtI$	–	≥ 175
	$EtONO_2H^+ + EtI \rightarrow EtIH^+ + EtONO_2$	+	
Cyclohexene	$EtONO_2H^+ + C_6H_{10} \rightarrow C_6H_{11}^+ + EtONO_2$	–	≤ 180
C_2H_5OH	$EtONO_2H^+ + EtOH \rightarrow EtOH_2^+ + EtONO_2$	–	≤ 183
C_2H_5CHO	$EtONO_2H^+ + EtCHO \rightarrow EtCHOH^+ + EtONO_2$	–	≤ 186
Propylene	$C_3H_7^+ + EtONO_2 \rightarrow EtONO_2H^+ + C_3H_6$	–	≥ 181
	$EtONO_2H^+ + C_3H_6 \rightarrow C_3H_7^+ + EtONO_2$	–	≤ 181
	$C_3H_6^+ + EtONO_2 \rightarrow EtONO_2H^+ + C_3H_5$	–	≥ 178
H_2S	$H_3S^+ + EtONO_2 \rightarrow EtONO_2H^+ + H_2S$	–	≥ 170
	$H_2S^+ + EtONO_2 \rightarrow EtONO_2H^+ + HS$	–	≥ 165
	$EtONO_2H^+ + H_2S \rightarrow H_3S^+ + EtONO_2$	+	
CH_3NO_2	$CH_3NO_2H^+ + EtONO_2 \rightarrow EtONO_2H^+ + CH_3NO_2$	–	≥ 179
CH_3COOH	$EtONO_2H^+ + CH_3COOH \rightarrow CH_3COOH_2^+ + EtONO_2$	–	≤ 185
CH_3CN	$EtONO_2H^+ + CH_3CN \rightarrow CH_3CNH^+ + EtONO_2$	–	≤ 185

From thermochemical considerations the relations

$$PA(M) = \Delta H_f(M) + \Delta H_f(H^+) - \Delta H_f(MH^+)$$

$$HA(M^+) = \Delta H_f(M^+) + \Delta H_f(H) - \Delta H_f(MH^+)$$

$$PA(M) - HA(M^+) = IP(H) - IP(M)$$

are obtained, where IP (M) is the ionization potential of species M. The hydrogen affinity of M^+ is of interest since it is the hydrogen bond strength in the ion M^+H.

Limits on the proton affinity of a species M can be determined by observing reactions of the type

$$M_1H^+ + M_2 \rightleftarrows M_1 + M_2H^+$$

in which the proton affinity of either the neutral reactant or product is known.[8]

The proton transfer reactions observed in ethyl nitrate mixtures are given in Table III together with the sign of the double resonance signal (dk/dE_{ion}) and the limit which the reaction places on PA ($EtONO_2$). The reactions which provide the closest limits for the proton affinity of ethyl nitrate are

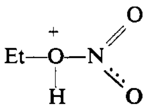
$$EtONO_2H^+ + c\text{-}C_6H_{10} \longrightarrow C_6H_{11}^+ + EtONO_2$$
$$\Delta H_f(EtONO_2H^+) \geq 149 \text{ kcal/mol}$$

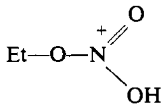
and

$$CH_3NO_2{}^+H + EtONO_2 \longrightarrow EtONO_2H^+ + CH_3NO_2$$
$$\Delta H_f(EtONO_2H^+) \leq 150 \text{ kcal/mol}$$

which give $\Delta H_f(EtONO_2H^+) = 149 \pm 3$ kcal/mol, PA($EtONO_2$) = 180 ± 3 kcal/mol, and HA($EtONO_2^+$) = 125 ± 3 kcal/mol.

Using a semiempirical SCF MO (MINDO method) theory, Dewar, *et al.*,[10] have calculated the heats of formation of two different forms (I and II) of protonated ethyl nitrate. They obtained values of 139 and 159


I


II

kcal/mol for the heats of formation of ions I and II, respectively. The experimental value of 149 kcal/mol is exactly halfway between these values and thus provides no basis for preferring one over the other. However, the fact that $H_2NO_3^+$ transfers NO_2^+ to ethyl nitrate (reaction 2, Table II) supports the conclusion of Dewar, *et al.*,[10] that protonated nitrates have structures of type I.

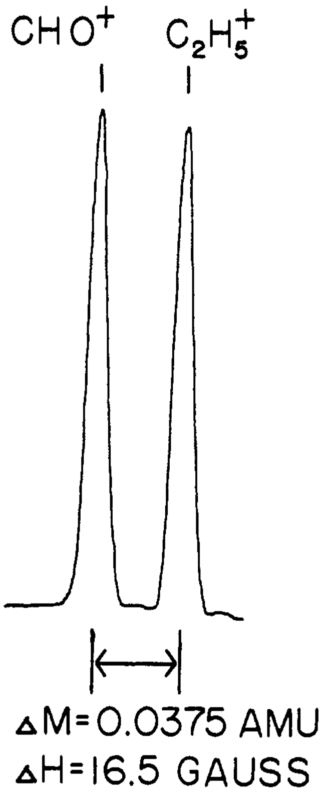


Figure 1. High resolution spectrum of the *m/e* 29 region in ethyl nitrate, taken with an observing marginal oscillator frequency of 691 kHz. The CHO^+ and $C_2H_5^+$ ion peaks are clearly resolved.

It is possible that a reactant ion may contain enough internal excitation energy to undergo reactions which would be endothermic for ground state ions. This possibility can be a source of uncertainty in the determination of proton affinities if the reactant ion is a fragment of one of the neutral molecules. However,

Table IV. Proton Affinities and Heats of Formation

		Positive Ions				
Species M	ΔH_f (M)	ΔH_f (M^+)	ΔH_f (MH^+)	PA (M)	HA (M^+)	Ref
H	52.1	366	356	62	62	*i*, *a*, *a*
CH_3I	3.3	223	199	170	77	*i*, *a*, *k*
CH_3OH	−48	202	142	175	112	*c*, *a*, *q*
CH_3CH_2I	−2.1	213	189	175	77	*i*, *a*, *k*
Cyclohexene	−0.84	199	185	180	66	*c*, *a*, *a*
CH_3CH_2OH	−56.2	185	127	183	111	*c*, *a*, *q*
CH_3CH_2CHO	−45.6	181	134	186	99	*c*, *a*, *b*
Propylene	4.88	229	190	181	91	*c*, *a*, *a*
C_3H_5 (allyl)	40.6	216	229	178	39	*i*, *a*, *a*
CH_3CN	19.1	300	200	185	152	*c*, *a*, *o*
H_2S	−4.8	235	191	170	96	*i*, *a*, *l*
HS	34	276	235	165	93	*i*, *a*, *a*
CH_3COOH	−103.8	135	77	185	110	*c*, *a*, *d*
CH_3NO_2	−17.9	238	167	179	123	*i*, *a*, *m*
$CH_3CH_2ONO_2$	−36.8	222	149	180	125	*c*, *a*, *n*
HNO_3	−32.1	222	(166)	(168)	(108)	*c*, *e*, *j*
CH_3O	3.5		202	168		*i*, *a*
CH_2O	−27.7		169	169		*i*, *b*
C_2H_2	54.19	317	269	151	100	*c*, *a*, *a*
C_2H_4	12.5	253	219	160	86	*c*, *a*, *a*
CO	−26.4	297	221	119	128	*a*, *a*, *a*
NO_2	7.91	234	222	152	64	*c*, *f*, *e*

		Negative Ions			
Species M	ΔH_f (M)	ΔH_f (M^-)	ΔH_f (MH)	PA (M^-)	Ref
NO_2	7.91	−82	−18.6	303	*c*, *h*, *c*
C_2H_5O	−4	−43	−56.2	379	*i*, *g*, *c*
Cl	29.08	−58.8	−22.06	329	*a*, *a*, *a*
OH	9.31	−33.67	−57.80	390	*a*, *a*, *a*
CH_3O	3.5	−30	−48.0	384	*i*, *p*, *c*
$(CH_3)_2CHO$	−12.6	−53	−65.2	378	*i*, *g*, *c*

[a] Reference 12. [b] K. M. A. Refaey and W. A. Chupka, *J. Chem. Phys.*, **48,** 5205 (1968). [c] Reference 11. [d] M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, **68,** 3191 (1964). [e] A. J. C. Nicholson, *J. Chem. Phys.*, **43,** 1171 (1965). [f] Reference 2. [g] J. M. Williams and W. H. Hamill, *J. Chem. Phys.*, **49,** 4467 (1968). [h] G R. Freeman, *Radiat. Res. Rev.*, **1,** 1 (1968) [i] S. W. Benson, "Thermochemical Kinetics," John Wiley and Sons, Inc., New York, N Y., 1968. [j] Reference 10, MINDO SCF MO calculation. [k] J. L. Beauchamp, Ph.D. Thesis, Harvard University, Oct 1967, estimate ±6 kcal/mol. [l] M. H. Haney and J. L. Franklin, *J. Chem. Phys.*, **50,** 2028 (1969). [m] Reference 5. [n] This work. [o] T. F. Moran and W. H. Hamill, *J. Chem. Phys.*, **39,** 1413 (1963). [p] Estimated from the relative acidities EtOH > MeOH > H_2O from ref 14. See text. [q] Reference *k*, determined from proton transfer reactions.

if the reactant ion is a protonated neutral molecule, then the reverse proton transfer reaction is also possible. Observation of both the forward and reverse of a proton transfer reaction proves that at least one of the protonated molecules is excited. Conversely, if the proton transfer reaction is observed in only one direction, it is very probable that it is exothermic for ground state ions, even if the reactant ion is internally excited.

All of the proton transfer reactions shown in Table III are consistent with $\Delta H_f(\mathrm{EtONO_2^+}) = 149$ kcal/mol, except for the reaction in the propylene mixture

$$C_3H_7^+ + EtONO_2 \longrightarrow EtONO_2H^+ + C_3H_6$$
$$\Delta H_f(EtONO_2H^+) \leq 148 \text{ kcal/mol} \quad (7)$$

However, the reverse reaction (8) was also observed

$$EtONO_2H^+ + C_3H_6 \longrightarrow C_3H_7^+ + EtONO_2$$
$$\Delta H_f(EtONO_2H^+) \geq 148 \text{ kcal/mol} \quad (8)$$

with negative (dk/dE_{ion}). Reaction 7 is therefore endothermic for ground state $C_3H_7^+$ ions.

The heats of formation and proton affinities used in this work are collected in Table IV. The references refer respectively to the first three columns of the table. The recent review by Benson, *et al.*,[11] of the heats of formation of nentral molecules, and the review by Franklin, *et al.*,[12] of the heats of formation of positive ions were the principal sources of these values. Realistic limits of error for the proton and hydrogen affinities of positive ions are approximately ±4 kcal/mol.

C. Negative Ions. The ICR negative ion spectrum of ethyl nitrate at approximately 1 eV contains five peaks corresponding to the ions NO_2^- (*m*/*e* 46), $C_2H_3O^-$ (*m*/*e* 43), $C_2H_5O^-$ (*m*/*e* 45), OH^- (*m*/*e* 17), and HNO_2^- (*m*/*e* 47), with relative intensities 100:12:1.7:1.1:0.6. These relative intensities agree qualitatively with the results of Jäger and Henglein;[4] a quantitative comparison is not possible because the ionization efficiencies are a strong function of electron energy from 0 to 1 eV.

The only negative ion-molecule reaction product in pure ethyl nitrate is NO_3^-. This is in agreement with the work of Jäger and Henglein, who observed an ion current at *m*/*e* 62 which was proportional to the square of the source pressure. ICR double resonance experiments show that NO_3^- is formed by reactions of $C_2H_3O^-$, $C_2H_5O^-$, and OH^- with ethyl nitrate.

The negative ion-molecule reactions occurring in mixtures of ethyl nitrate with a number of different compounds were examined in order to obtain information about the structure, reactivity, and internal energy of the negative fragment ions. All of the negative ion-molecule reactions observed are listed in Table V together with their thermodynamic implications. All of the negative ion-molecule reactions had negative double resonance signals (dk/dE_{ion}). The heats of formation used in obtaining the results in Table V are given in Table IV.[13]

---

(11) S. W. Benson, *et al.*, *Chem. Rev.*, **69,** 279 (1969).

(12) J. L. Franklin, *et al.*, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, National Bureau of Standards, Washington, D. C., June 1969.

Table V. Negative Ion-Molecule Reactions Observed in Ethyl Nitrate Mixtures

$EtONO_2$ mixed with	Reaction observed	Thermochemical[a] inference
	$C_2H_3O^- + EtONO_2 \rightarrow NO_3^- + C_4H_8O$	
	$C_2H_5O^- + EtONO_2 \rightarrow NO_3^- + Et_2O$	$\Delta H_f\,(NO_3^-) \leq -20$[b]
	$OH^- + EtONO_2 \rightarrow NO_3^- + EtOH$	$\Delta H_f\,(NO_3^-) \leq -14.3$[b]
Acetone	$OH^- + CH_3COCH_3 \rightarrow CH_3COCH_2^- + H_2O$	$\Delta H_f\,(CH_3COCH_2^-) \leq -28$
	$C_2H_5O^- + CH_3COCH_3 \rightarrow CH_3COCH_2^- + EtOH$	$\Delta H_f\,(CH_3COCH_2^-) \leq -39$
CH_3OH	$OH^- + CH_3OH \rightarrow CH_3O^- + H_2O$	$\Delta H_f\,(CH_3O^-) \leq -23.9$
CD_3OH	$CD_3O^- + EtONO_2 \rightarrow NO_3^- + EtOCD_3$	
C_2D_5OH	$C_2D_5O^- + EtONO_2 \rightarrow NO_3^- + EtOC_2D_5$	$\Delta H_f\,(NO_3^-) \leq -20$[b]
	$OH^- + C_2D_5OH \rightarrow C_2D_5O^- + H_2O$	$\Delta H = -11$
Isopropyl alcohol	$C_2H_5O^- + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7O^- + EtOH$	$\Delta H = -4$
	$OH^- + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7O^- + H_2O$	$\Delta H = -6.5$
CH_3CH_2CHO	$C_2H_5O^- + EtCHO \rightarrow C_3H_5O^- + EtOH$	$\Delta H_f\,(C_3H_5O^-) \leq -36$
	$C_2H_3O^- + EtCHO \rightarrow C_3H_5O^- + C_2H_4O$	
	$OH^- + EtCHO \rightarrow C_3H_5O^- + H_2O$	$\Delta H_f\,(C_3H_5O^-) \leq -24.6$
	$HNO_2^- + EtCHO \rightarrow C_3H_5O^- + (H_2NO_2)$	
n-Propyl chloride	$OH^- + n\text{-}PrCl \rightarrow Cl^- + C_3H_7OH$	$\Delta H = -56.3$[b]
	$C_2H_5O^- + n\text{-}PrCl \rightarrow Cl^- + C_3H_7OC_2H_5$	$\Delta H = -50$[b]

[a] In kcal/mole. [b] Assuming the neutral products are those expected from a displacement reaction.

Most of the reactions were proton transfers. A previous study[14] of proton transfer reactions in the alcohols showed that the relative basicities or proton affinities of the alkoxide ions were $OH^- > MeO^- > EtO^- > i\text{-}PrO^-$. In complete agreement with that result the authors observed the reactions

$$OH^- + MeOH \longrightarrow MeO^- + H_2O \tag{9}$$

$$OH^- + i\text{-}PrOH \longrightarrow i\text{-}PrO^- + H_2O \tag{10}$$

$$EtO^- + i\text{-}PrOH \longrightarrow i\text{-}PrO^- + EtOH \tag{11}$$

in mixtures of ethyl nitrate with methanol and isopropyl alcohol. There are very few experimental values for the heats of formation of alkoxide ions. Williams and Hamill[15] recently reported electron affinities for ethoxide and isopropoxide radicals which yield $\Delta H_f\,(EtO^-) = -43$ and $\Delta H_f\,(i\text{-}PrO^-) = -53$ kcal/mol. These values are consistent with reactions 9-11 and with all of the reactions reported by Brauman and Blair.[14]

Reaction 9, together with reaction 12, observed by

$$MeO^- + EtOH \longrightarrow EtO^- + MeOH \tag{12}$$

Brauman and Blair, implies that $-35 \leq \Delta H_f\,(MeO^-) \leq -24$ kcal/mol. As with positive ions, observation of a negative ion-molecule reaction does not guarantee that the reaction is exothermic for ground state ions. The possible presence of excited ions must not be ignored in deriving heats of formation from the observation of ion-molecule reactions. The fact that no reactions of OH^- or EtO^- were observed which are inconsistent with the heats of formation in Table V, together with the fact that all exothermic reactions were observed, suggests that excited ions are not involved in these alkoxide ion reactions. Therefore, a value of $\Delta H_f\,(MeO^-) = -30 \pm 6$ kcal/mol has been assigned.

The negative ion reactions in a mixture of ethyl nitrate and C_2D_5OH were examined to check the amount of internal energy in the EtO^- ion from ethyl nitrate. The reaction

$$C_2H_5O^- + C_2D_5OH \longrightarrow C_2D_5O^- + C_2H_5OH$$

could not be detected using the double resonance technique. This result indicates that very few, if any, of the $C_2H_5O^-$ ions are excited.

While most of the negative ion-molecule reactions observed were proton transfer reactions, several displacement-like reactions were found. Hydroxide and ethoxide ions were capable of displacing chloride from *n*-propyl chloride, while hydroxide, methoxide, ethoxide, and $C_2H_3O^-$ ions could displace NO_3^- from ethyl nitrate. It must be stressed that these reactions *appear* to be displacement reactions; a displacement mechanism cannot be proved unless the neutral product can be identified. The chloride displacement-like reactions were sufficiently exothermic that several different choices of neutral products are thermochemically possible. For example, the reaction

$$EtO^- + n\text{-}PrCl \longrightarrow Cl^- + n\text{-}PrOEt$$

is 50 kcal/mol exothermic, but if the neutral products are ethanol and propylene instead of *n*-propyl ethyl ether, the reaction is still exothermic by 36 kcal/mol.

D. Electron Impact Excitation Spectra. Certain compounds such as SF_6, CH_3I, CCl_4, and ethyl nitrate have large cross sections for thermal energy electron capture. This fact has been used by Curran,[16] Compton, *et al.*,[17] and Jacobs and Henglein[18] to study the low energy electron impact excitation of a number of simple molecules. When the incident electron energy is just equal to the excitation energy of the molecule, an inelastic collision can produce an electronically excited molecule and a near zero energy electron. The scattered electrons are captured by the scavenger molecules and detected by measuring the resulting negative ion current. Ridge and Beacuchamp[19] have recently demonstrated that the ICR spectrometer is well suited to this type of experiment. The scattered electrons are confined by the trapping fields just as are the negative ions. The residence time of low energy electrons can be 10 msec or more. This allows a very low concentration of scavenger to be used and avoids errors produced by excitation of the scavenger molecules.

---

(13) Additional heats of formation used in these calculations were taken from ref 11. They are ΔH_f (MeOMe) = −51.7, ΔH_f (CH_2-CHCN) = 43.7, ΔH_f (*n*-PrCl) = −31.2, ΔH_f (*n*-PrOH) = −61.3, ΔH_f (EtOEt) = −60.3, ΔH_f (MeOEt) = −51.7, and ΔH_f (*n*-PrOEt) = −65.5, all in units of kcal/mol.

(14) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 6561 (1968).

(15) Reference *g*, Table IV.

(16) R. K. Curran, *J. Chem. Phys.*, **38**, 780 (1963).

(17) R. N. Compton, R. H. Huebner, P. W. Reinhardt, and L. G. Christophorou, *ibid.*, **48**, 901 (1968).

(18) G. Jacobs and A. Henglein, *Advan. Mass Spectrom.*, **3**, 287 (1966).

(19) D. P. Ridge and J. L. Beauchamp, *J. Chem. Phys.*, **51**, 470 (1969).

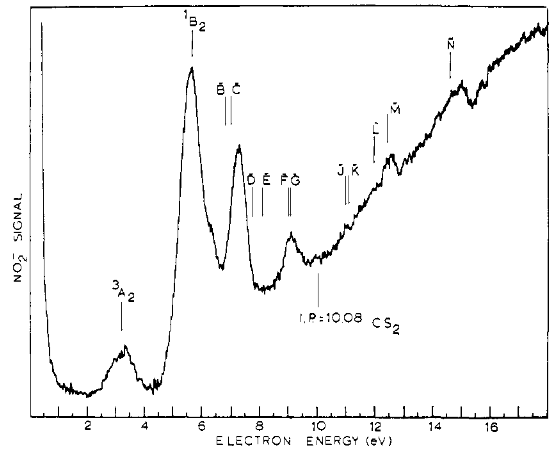


Figure 2. Low energy electron inelastic excitation spectrum of carbon disulfide. Ethyl nitrate was used to detect thermal energy electrons by monitoring the NO_2^- ion signal.

Ridge and Beauchamp[19] used CCl_4 as a slow electron detector and monitored the Cl^- signal produced by the reaction

$$e^-_{\text{thermal}} + CCl_4 \longrightarrow Cl^- + CCl_3$$

The authors have found that carbon tetrachloride is difficult to work with because of a large Cl^- background signal, presumably produced by surface ionization of CCl_4 absorbed on the filament. The reaction

$$e^-_{\text{thermal}} + EtONO_2 \longrightarrow NO_2^- + EtO\cdot$$

has a cross section of about 240×10^{-16} cm^2 for thermal energy electrons.[4] Figure 2 shows an electron energy excitation spectrum of carbon disulfide obtained using the NO_2^- ion signal from ethyl nitrate to monitor the number of thermal energy electrons produced. The known electronic energy levels are indicated using the designations given by Herzberg.[20] All of the peaks correspond to known spectroscopic states of CS_2 with the exception of the large peak at 7.3 eV. Jacobs and Henglein[18] also saw a large peak at this energy using both SF_6 and CH_3I as electron scavengers. The complete absence of a residual or background signal above an electron energy of 1.5 eV and the large cross section for NO_2^- formation (20 times larger than the most commonly used process, SF_6^- from SF_6) make ethyl nitrate an excellent detector for thermal energy ions.

Acknowledgments. One of us (S. E. B.) wishes to thank Professor John D. Baldeschwieler of Stanford for his enthusiasm and encouragement, and the National Science Foundation for a Graduate Fellowship. Support of the National Science Foundation under Grant No. GP-4924-X, the National Aeronautics and Space Administration under Grant No. NGL-05-020-250, and the Center for Materials Research at Stanford University is gratefully acknowledged.

---

[20] G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1966, pp 601-602 and p 594.

Chemiluminescence from Peroxide Decomposition Reactions. The Role of Energy Transfer[1a]

Seth R. Abbott, Stanley Ness, and David M. Hercules[1b]

Contribution from the Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Received August 28, 1969

Abstract: Chemiluminescence from thermal decomposition of dibenzal diperoxide in the presence of aromatic fluorescent compounds was studied. The emitting species was identified as the lowest excited singlet state of the aromatic fluorescer. The excitation step producing this species was shown to involve energy transfer from excited state species produced by the peroxide decomposition, *i.e.*, triplet benzaldehyde and/or singlet oxygen monomers and collisional pairs. Energy transfer from the benzaldehyde triplet was shown to be due to a long-range dipole–dipole interaction in solution. Energy transfer from singlet oxygen monomers, occurring through a two-step mechanism involving the fluorescer triplet as an intermediate, was shown to be more significant than transfer from singlet oxygen collisional pairs.

Addition of dibenzal diperoxide to a paraffin oil solution of dibenzanthrone at 200° was observed by Kurtz to produce red chemiluminescence.[2a] Kurtz proposed a mechanism involving[2a] thermal decomposition of the peroxide, producing oxygen[2b] addition to dibenzanthrone,[3] rapid dissociation of the *endo*-peroxide to ground state oxygen, and emission form the dibenzanthrone triplet state.

We have identified the emitting species in this system as the lowest excited singlet state of dibenzanthrone by matching the chemiluminescence (CL) and fluorescence spectra. The chemiluminescence spectrum was obtained using a fast image-intensifier spectrograph.[2b]

The question remained as to how the emitting species was produced. Benzaldehyde and oxygen were shown to be the products of peroxide decomposition.

---

[1] (a) Paper presented at the International Conference on Chemiluminescence, Desert Hot Springs, Calif., March 1969; (b) address all correspondence to this author at the Department of Chemistry, University of Georgia, Athens, Ga. 30601.

[2] (a) R. B. Kurtz, *Ann. N. Y. Acad. Sci.*, 16, 399 (1954); (b) S. Ness and D. M. Hercules, *Anal. Chem.*, **41**, 1467 (1969).

[3] M. M. Rauhut, *Accounts Chem. Res.*, **2**, 80 (1969).