tally by the usual procedure. The dielectric constants were ϵ_{15° 200.1, ϵ_{25° 182.4, ϵ_{35° 174.3, and ϵ_{45° 167.1 at the temperatures indicated and were those reported by Leader and Gormley.[7] The values of viscosities at the different temperatures were $\eta_{15^\circ} = 0.0199$, $\eta_{25^\circ} = 0.0165$, $\eta_{35^\circ} = 0.0142$, and $\eta_{45^\circ} = 0.0123$ poise.[6,8] The values of the limiting transport numbers, t_+^0, of K^+, at various temperatures, obtained from the plot of the Longsworth function against concentration, are also given in Table I under the concentration heading 0.00 *M*.

Results and Discussion

As can be seen from Table I, the variations in the transport number, t_+, of K ion in N-methylformamide are very much similar to those in formamide[3] and in N-methylacetamide;[4] *i.e.*, t_+ decreases with increase in concentration and increases with increase in temperature. The limiting transport number of potassium ion, *i.e.*, $t_+^\circ{}_{(K^+)}$, increases from 0.4945 at 15° to 5290 at 45°. This behavior is opposite to that in aqueous solutions in which $t_+^\circ{}_{(K^+)}$ decreases slightly with rise in temperature. Recently, Gill[9] has reported similar behavior of the cationic transport number of KNO_3 in liquid ammonia in which $t_+^\circ{}_{(K^+)}$ has been found to decrease with rise in temperature in the range −65 to −45°, although $t_+^\circ{}_{(Na^+)}$, $t_+^\circ{}_{(Li^+)}$, and $t_+^\circ{}_{(NH_4^+)}$ increase with rise in temperature as $t_+^\circ{}_{(K^+)}$ (KBr) does in N-methylformamide.

It may be noted that $t_+^\circ{}_{(K^+)}$ increases beyond 0.5 with rise in temperature. This is a little unusual although such values of the transport number have been reported in the literature.[10]

Ionic Mobilities

The limiting cationic transport numbers at different temperatures can be used to calculate the ionic mobilities from the available electrolytic conductance data[6] in this solvent and making use of the usual Kohlrausch law of the independent migration of ions. The ionic conductivities at infinite dilution of some ions thus obtained are given in Table II.

Table II: Mobilities of Some Ions in N-Methylformamide at Different Temperatures

Ion	Ionic mobility at 15°	25°	35°	45°
Na^+	17.59	21.56	...	...
K^+	18.05	22.13	27.62	32.15
Cs^+	19.90	24.39	...	...
$(C_2H_5)_4N^+$	21.52	26.20	...	...
$Picrate^-$	11.28	13.08	...	...
Cl^-	16.88	19.70	...	...
Br^-	18.46	21.56	25.38	28.60
I^-	19.38	22.76	...	...

Since no ionic conductance data are available in the literature, it is not possible to verify the values given in Table II. However, they seem to be reasonable if they are compared with the corresponding values in formamide and in N-methylacetamide. Since the tetrahedral structure present in water is missing in these solvents, the structure-breaking effect of the larger ions like K^+ is also missing in these solvents and so all the ions behave normally. In view of the lack of sufficient and appropriate electrolytic, and hence the ionic, conductance data in this solvent, it is not possible to make a reasonable estimate of the solvation of ions as was done in NMA.[4] This aspect will be examined later when the required data are available.

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Photooxidation of Perfluoroethyl Iodide and Perfluoro-*n*-propyl Iodide[1a]

by Dana Marsh and Julian Heicklen[1b]

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In earlier reports, the oxidation of CF_3[2] and $CFCl_2$[3] radicals was examined. In the former case, the only carbon-containing product was CF_2O, whereas in the latter case only CFClO was found. In the presence of HI, the results were unchanged.

In this work, we extend the oxidation studies to C_2F_5 and n-C_3F_7 radicals in order to determine the products of reaction and the nature of the intermediates. In both cases, the major product is CF_2O.

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(1) (a) This work was supported by the U. S. Air Force under Contract No. AF 04(695)-669. (b) To whom requests for reprints should be sent.

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In the C_2F_5I system, it is produced with a quantum yield of about 2.0. CF_3CFO is also produced, but is only $^1/_{40}$ as important. With HI present, the oxidation is drastically modified, and the RO_2 intermediate must live at least 10^{-7} sec.

Experimental Section

Perfluoroethyl iodide and perfluoro-*n*-propyl iodide were obtained from Peninsular ChemResearch, Inc. Gas chromatographic analysis showed no impurities in the C_2F_5I but one major impurity of about 7% in the *n*-C_3F_7I. The C_2F_5I was used after degassing at −196°, but the C_3F_7I was purified by trap-to-trap fractionation, and that fraction volatile at −63.5° but condensable at −126° used. In this way, the impurity level was reduced but not eliminated. Furthermore, the violet color of the impure material disappeared. Matheson research grade O_2 and anhydrous HI (degassed at −196°) were used.

Infrared analyses were performed *in situ* in a Perkin-Elmer Model 13 Universal spectrometer. A T-shaped cell was used, having 11.5-cm infrared and 10.7-cm ultraviolet path lengths. The ultraviolet light entered the stem of the T through a quartz window. The top of the T had sodium fluoride windows at each end and was situated in the infrared beam. Radiation was from a Hanovia-type SH, U-shaped mercury lamp and passed through a Corning 0-53 glass to remove wavelengths below 2800 A before entering the cell. The effective radiation was primarily at 3130 A with the line at 3020 A also playing some role.

The ultraviolet absorption coefficients for HI, C_2F_5I, and C_3F_7I were determined at 3020 and 3130A on a Cary Model 15 spectrophotometer. For longer wavelengths (*i.e.*, 3340 A and above) there was no absorption. Absolute quantum yields were measured by comparison with the CF_2O produced from photolysis of CF_3I–O_2 mixtures where $\Phi(CF_2O) = 1.0$.

Results and Discussion

The photolysis of C_2F_5I or C_3F_7I yields no products, even for extended exposures. As in all alkyl iodides, the indicated mechanism is

$$RI + h\nu \longrightarrow R + I \tag{1}$$

$$2R \longrightarrow R_2 \tag{2}$$

$$R + I \longrightarrow RI \tag{3}$$

$$2I + M \longrightarrow I_2 \tag{4}$$

However, the I_2 is a powerful radical scavenger, and very quickly the reaction is inhibited by

$$R + I_2 \longrightarrow RI + I \tag{5}$$

With C_2F_5I–O_2 mixtures, the products found were CF_2O, CF_3CFO, and SiF_4. Iodine is also formed and perhaps F_2 or F_2O, though they would not be detected by infrared analysis. The rate of SiF_4 formation increases with exposure time, indicating secondary decomposition of some product. However, the CF_3CFO and CF_2O grow linearly with time; their quantum yields are listed in Table I. The C_2F_5I and O_2 pressures were varied from 10 to 300 mm, but the quantum yields were unaffected. They are $\Phi(CF_2O) = 2.0$ and $\Phi(CF_3CFO) = 0.05$. The mechanism that most easily explains the results is

Table I: Photooxidation of C_2F_5I
($T = 25°$, $I_0 = 35 \pm 5\ \mu$/min)

(C_2F_5I), mm	(O_2), mm	$\Phi(CF_2O)$	$\Phi(CF_3CFO)$
11	10	2.1	0.072
10	300	2.0	0.054
31	10	1.4	0.040
28	33	2.7	0.072
28	265	1.6	0.035
100	10	1.7	0.069
102	127	2.1	0.051
100	300	1.9	0.043
315	10	. . .	0.056
300	315	2.2	0.024
300	362	4.8	0.069
		Av 2.0 ± 0.3	0.053 ± 0.013

$$C_2F_5 + O_2 \longrightarrow C_2F_5O_2 \tag{6}$$

$$C_2F_5O_2 \longrightarrow CF_2O + CF_3O \tag{7}$$

$$C_2F_5O_2 \longrightarrow CF_3CFO + FO \tag{8}$$

where k_7/k_8 is about 20. The CF_3O formed from (7) may have sufficient energy to decompose immediately

$$CF_3O^* \longrightarrow CF_2O + F \tag{9}$$

or it may form CF_2O by

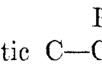
$$2CF_3O \longrightarrow 2CF_2O + F_2 \tag{10}$$

With C_3F_7I–O_2 mixtures, the results are more difficult to interpret because of the presence of the impurity. The products observed were the same as in the C_2F_5I–O_2 photolysis. Initially, the unpurified C_3F_7I was irradiated and CF_2O was produced with a quantum yield of from 10 to 30. Purification of the C_3F_7I by fractionation reduced the impurity level considerably, but did not eliminate the impurities. Photolysis of mixtures of O_2 and the purified C_3F_7I showed the initial large $\Phi(CF_2O)$, but the rate of CF_2O production rapidly dropped to a smaller constant value as the CF_2O approached about 1% of the C_3F_7I. Presumably, the initial reaction is similar to that for C_2F_5 radicals

$$C_3F_7 + O_2 \longrightarrow C_3F_7O_2 \qquad (11)$$

In some manner, the $C_3F_7O_2$ radical must yield primarily CF_2O. How this occurs is not clear at all.

It is of interest to know whether the RO_2 radical has a measurable lifetime. To that end, we did a number of experiments with 5 to 40 mm of HI added. Two series of experiments were done, one with 280 mm of C_2F_5I and 300 mm of O_2, and the other with 100 mm of C_3F_7I and 300 mm of O_2. Hydrogen iodide had no effect at all on CF_3 or $CFCl_2$ oxidation.[2,3] However, with C_2F_5 and C_3F_7, very marked changes occurred in the oxidation. The results, the same for both series, showed no trend with HI pressure, thus indicating that the initially formed perfluoroalkyl radical was completely scavenged by O_2.

The results can be summarized as follows. First, a red deposit was formed. Second, $\Phi(CF_2O)$ was reduced at least 5- to 20-fold. Third, $\Phi(CF_3CFO)$ may have increased to 0.13 to 0.30 for C_2F_5 radicals as based on the 9.05-μ band of CF_3CFO. The analysis is difficult because of the HI absorption in this region. Fourth, the characteristic  $\mathrm{C{-}\overset{F}{C}{=}O}$ band at 5.31 μ was the most intense band and was formed at the same rate in all experiments with HI. The CF_3CFO can account for only 25 to 50% of the 5.31-μ band in the C_3F_7I series, but perhaps all of it in the C_2F_5I series. At least for the C_3F_7I series, another product probably was formed. There can be no doubt that HI interferes with the oxidation. Consequently, the RO_2 radical must have a lifetime in excess of 10^{-7} sec.

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Heats of Transport of the Rare Gases in a Rubber Membrane[1]

by Mirion Y. Bearman and Richard J. Bearman

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Revised values for the heats of transport, Q^*, of the rare gases He, Ne, Ar, Kr, and Xe in rubber are presented. In the case of helium, it is shown that, within experimental error, there is no pressure dependence of the heat of transport in the pressure range 25–65 cm. The apparent Q^* varies slightly with temperature difference across the membrane. Nevertheless, departures from linearity in the local phenomenological equations seem to be negligible even though the temperature gradients range up to 900°/in.

Revised Heats of Transport (Q^*)

In an earlier article, Bearman[2] reported the heats of transport (or "transfer"), Q^*, of the rare gases in a rubber membrane. His values were obtained from thermoosmosis experiments where, at steady state

$$\ln (p_H/p_C)_\infty = -(Q^*/R)(1/T_C - 1/T_H) \qquad (1)$$

Here, H and C refer to the hot and cold side, respectively, T is absolute temperature, p is pressure, and R is the gas constant. His measurements were subject to several errors of unknown magnitude arising chiefly from uncertainties in the pressure and temperature.

With the use of strain gauge pressure transducers and several thermocouple probes, we have constructed an improved apparatus, fully described elsewhere,[3,4] in which the errors have been greatly lowered. In Table I, we present revised values for the heats of transport together with a comparison with the earlier results. The error estimates take into account the observed irreproducibility and also errors arising from temperature and pressure measurements. The irreproducibility is caused mostly by leakage, degassing, and adsorption in the system[3] over the long course of the runs, which last days or sometimes weeks. A pure gum rubber membrane 0.0325 to 0.0350 cm in thickness was used for our measurements reported here.

Pressure and Temperature Difference Dependence of Q^*

Some additional measurements were made with helium. In Table II, we show that, within the experimental error, the heat of transport at constant mean temperature and temperature difference is independent of mean gas pressure in the system in the range from 25 to 65 cm. From this, we conclude that the He–He interactions in the membrane play little role

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