

that the radiation-induced polymerization of ethylene at ambient temperature is adequately described by a free-radical mechanism.

(7) *The Role of Neutralization.* In the preceding discussion, charge neutralization has been ignored completely. The use of electron attachment coefficients for ethylene or oxygen^{21,29} allows one to predict that $C_2H_4^-$ will not be formed under our experimental conditions. Since the positive charge survives more than 10^4 collisions, neutralization by free electrons will occur when it resides either on a highly complex polymeric ethylene unit as formed by reactions 12 and 13, or on a highly unsaturated radical as formed by reaction 10 and its higher analogs. In either case the resultant, neutralized species would be of such a complexity that it would not be detectable by the experimental techniques employed in this investigation.

Since free-radical-induced polymerization is insignificant under our conditions, one can estimate the extent of the contribution of ionic processes from the lack of material balance. The products listed in Table I account for 61.5% of the consumed ethylene units (carbon balance); the missing components have an average empirical composition $C_nH_{1.7n}$, supporting the conclusion that neutralization involves highly complex and unsaturated species.

Conclusions

The most important primary radical in the radiolysis of ethylene is the hydrogen atom. Its reactions and those of its sequent radicals largely determine the dose rate and pressure dependence of all products which have simple radicals as precursors. An approximate kinetic scheme can be employed to arrive at a quantitative description of the yield dependence on kinetic parameters. Other primary radicals, formed without radical addition to ethylene, include methyl, *n*-propyl, *sec*-propyl, and *sec*-butyl radicals. Their formation must be ascribed to higher order ion-molecule reactions.

A molecular mechanism is established for the formation of the butenes and cyclobutane. Higher order ionic association steps are suggested as an explanation for the former, while dimerization of an excited species is invoked to interpret the formation of the latter.

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Free Radicals by Mass Spectrometry.

XXXIII. Ionization Potentials of CF_2 , CF_3CF_2 , CF_3CH_2 , *n*- C_3F_7 , and *i*- C_3F_7 Radicals

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*The vertical ionization potentials of three perfluoralkyl radicals are found to be 9.98, 10.06, and 10.5 v. for C_2F_5 , *n*- C_3F_7 , and *i*- C_3F_7 , respectively. The increase in ionization potential with CF_3 substitution is in contrast with the decrease found along the alkyl series and accounts for certain features of the mass spectra of perfluoroparaffins. These results suggest that $I(CF_3)$ should be <9.5 v. and that $I_{vert}(CF_3) = 10.1$ v. measured by direct electron impact includes >0.6 v. of excitational energy. $I(CF_3CH_2)$ is found to be 10.6 v., appreciably higher than $I(CF_3CF_2)$. The CF_2 radical has been produced by the thermal decomposition of the C_2F_5 radical, and $I_{vert}(CF_2)$ is 11.7 v. With appearance potential data this gives $\Delta H_f(CF_2) \sim -36$ kcal./mole.*

Introduction

Experimental measurements of the ionization potential of the CF_3 radical have fallen into two groups: values of 10.1–10.2 v. from direct electron impact on CF_3 radicals produced by thermal reactions in a mass spectrometer,^{2–4} and values of 8.9–9.5 v. from dis-

sociative ionization of CF_3 derivatives by the indirect electron impact method.^{5–7} The situation, with regard to the "high" and "low" values for $I(CF_3)$, the heats of formation of CF_3 and CF_3^+ derived from appearance potentials, and the thermodynamic properties of CF_3 derivatives, has been reviewed recently^{8–10} and will not be discussed here except to comment that, although the inconsistencies in the appearance potential data for CF_3^+ from different compounds are large, these data can more easily be reconciled with $I(CF_3) \sim 9.5$ v. than with $I(CF_3) \sim 10.1$ v.

It is difficult to predict on theoretical grounds

- (2) J. B. Farmer, I. H. S. Henderson, and F. P. Lossing, *J. Chem. Phys.*, **23**, 403 (1955).
- (3) R. I. Reed and W. Snedden, *Trans. Faraday Soc.*, **54**, 301 (1958).
- (4) F. P. Lossing, P. Kebarle, and J. B. de Sousa, "Advances in Mass Spectrometry," J. Waldron, Ed., Pergamon Press, Inc., New York, N. Y., 1959, p. 431.
- (5) V. H. Dibeler, R. M. Reese, and F. L. Mohler, *J. Chem. Phys.*, **20**, 1761 (1952).
- (6) V. H. Dibeler, R. M. Reese, and F. L. Mohler, *J. Res. Natl. Bur. Std.*, **57**, 113 (1956).
- (7) C. Lifshitz and F. A. Long, *J. Phys. Chem.*, **67**, 2463 (1963).
- (8) C. R. Patrick, *Advan. Fluorine Chem.*, **2**, 1 (1961).
- (9) J. R. Majer, *ibid.*, **2**, 55 (1961).
- (10) W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 3450 (1962).

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whether $I(\text{CF}_3)$ should be lower or higher than $I(\text{CH}_3)$. The stability of CF_3^+ , with respect to neutral CF_3 , will be the resultant of two opposing effects in the ion, the high inductive effect of the F atoms tending to raise the ionization potential and the effect of resonant ionic stabilization tending to lower it. These opposing effects, as discussed by Price, *et al.*,^{11,12} have magnitudes of several volts, and the resultant effect cannot be predicted with certainty. They concluded,¹¹ however, that the stabilization effect predominates in CF_3^+ and that $I(\text{CF}_3) \sim 9.5$ v. was to be preferred to the higher value.

It was thought that some clarification of the question of $I(\text{CF}_3)$ could be made by a comparison with the ionization potentials of perfluoroethyl and perfluoropropyl radicals. These measurements are described in the present work.

The ionization potential of the CF_2 radical has been remeasured, in view of the large discrepancy between the direct³ and indirect¹³ values.

Experimental

The radicals were generated in a fused-silica capillary furnace leading to the ionization chamber of a mass spectrometer.¹⁴ The method of evaluating the appearance potential curves has been described.¹⁵

C_2F_5 radicals were obtained in good yield from the thermal decomposition of $\text{C}_2\text{F}_5\text{N}=\text{NC}_2\text{F}_5$ at 800° at low pressures and millisecond contact times. The *n*- C_3F_7 radicals were similarly obtained from $\text{CF}_3\text{-CF}_2\text{CF}_2\text{N}=\text{NCF}_2\text{CF}_2\text{CF}_3$. The *i*- C_3F_7 radicals were prepared from $(i\text{-C}_3\text{F}_7)_2\text{Hg}$ at 820° . Attempts to prepare *t*- C_4F_9 radicals from $(t\text{-C}_4\text{F}_9)_2\text{Hg}$ were unsuccessful. This compound appeared to dissociate by a mechanism other than a simple C-Hg bond scission. Above 950° C_2F_5 radicals from $\text{C}_2\text{F}_5\text{N}=\text{NC}_2\text{F}_5$ were found to decompose to give CF_3 and CF_2 radicals in good abundance.

CF_3CH_2 radicals were prepared from $\text{CF}_3\text{CH}_2\text{N}=\text{NCH}_2\text{CF}_3$. A small amount of $\text{CF}_3\text{CH}_2\text{N}=\text{NC}_2\text{H}_5$ impurity was present in this sample, but the consequent formation of the C_2H_5 radical caused no difficulty with the measurements on CF_3CH_2 .

Results and Discussion

The vertical ionization potentials found for the C_2F_5 , CF_3CH_2 , and *n*- and *i*- C_3F_7 radicals are given in Table I. The measurements were reproducible within 0.1 v., but the probable error, if taken as the amount that these values may exceed the true adiabatic ionization potential, is unknown. It will be seen that $I(i\text{-C}_3\text{F}_7) - I(\text{C}_2\text{F}_5)$, the increase in ionization potential resulting from substitution of F by CF_3 , is 0.5 v. This substitution replaces the electrophilic F atom by an almost equally electrophilic CF_3 group but also replaces a C-F bond, capable of stabilization by C-F⁺ resonance, by a C-CF₃ bond which has no capability in this respect. For the present purposes, the over-all effect can be most conveniently discussed in terms of

substituent constants of the Hammett σ -type, which have been shown to be closely related to changes in free-radical ionization potentials.¹⁶⁻¹⁸ In terms of σ_I (inductive) and σ_R (resonance) values,¹⁹ the F atom has $\sigma_I = +0.52$ and $\sigma_R = -0.44$. These constants reflect the opposing effects of the F atom on ionization potentials discussed by Price, *et al.*¹¹ The CF_3 group has $\sigma_I = +0.41$ but a much different σ_R , +0.09. On these grounds one would expect the substitution of CF_3 for F to result in a considerable increase in ionization potential. This is borne out by the difference in the observed values for CF_3CF_2 and $(\text{CF}_3)_2\text{CF}$ radicals. The increase, 0.52 v., is virtually the same as that resulting from the corresponding substitution on a benzene nucleus, $I(\text{CF}_3\text{C}_6\text{H}_5) - I(\text{FC}_6\text{H}_5)$ being 0.48 v.²⁰ Similarly one would expect the difference, $I(\text{CF}_3\text{CF}_2) - I(\text{CF}_3)$, resulting from the same substitution to be also about 0.5 v. That is, $I_{\text{adiabatic}}(\text{CF}_3)$ should on this basis be 9.5 v., or less, if $I_{\text{vert}}(\text{CF}_3\text{CF}_2)$ includes excitational energy. The direct electron impact value of 10.1 v. for CF_3 seems, therefore, to be much too high to be compatible with the higher members of the series. It has been pointed out¹² that CF_3^+ is probably planar, but in neutral CF_3 the repulsion between the $p\pi$ -electron on the C atom and the $p\pi$ -electrons on the F atoms would cause CF_3 to be nonplanar. If the change in energy with departure from equilibrium configuration in CF_3 and CF_3^+ were sufficiently large, the vertical transition could include considerable energy in excess of the adiabatic ionization potential. Values of $\Delta H_f(\text{CF}_3^+)$ derived from dissociative ionization of CF_3X derivatives, on the other hand, would approach the adiabatic value if the equilibrium conformation of CF_3^+ were easily achieved in a dissociating CF_3^+-X ion in the relatively long time available.

Table I. Vertical Ionization Potentials of Radicals

Radical	Radical source	$I_{\text{vert.}}$ v.
$\text{CF}_3\dot{\text{C}}\text{F}_2$	$\text{CF}_3\text{CF}_2\text{N}=\text{NCF}_2\text{CF}_3$	9.98
$\text{CF}_3\text{CF}_2\dot{\text{C}}\text{F}_2$	$\text{CF}_3\text{CF}_2\text{CF}_2\text{N}=\text{NCF}_2\text{CF}_2\text{CF}_3$	10.06
$(\text{CF}_3)_2\dot{\text{C}}\text{F}$	$(\text{CF}_3)_2\text{CFHgCF}(\text{CF}_3)_2$	10.5
$\text{CF}_3\dot{\text{C}}\text{H}_2$	$\text{CF}_3\text{CH}_2\text{N}=\text{NCH}_2\text{CF}_3$	10.6
$\dot{\text{C}}\text{F}_2$	$\text{CF}_3\text{CF}_2\text{N}=\text{NCF}_2\text{CF}_3$	11.7

$I(\text{CF}_3) < 9.5$ v. is more easily reconciled with values of about 9.4 v. for CH_2F and CHF_2 radicals.⁴ By comparison with $I(\text{CH}_3) = 9.84$ v.,²¹ it appears that the inductive effect of the F atoms is overbalanced by the increase in resonance stabilization. This is also borne out by the difference $I(\text{CF}_3\text{CH}_2) - I(\text{CF}_3\text{CF}_2)$, which is 0.6 v. The effect of substituting CF_3 for H is more straightforward since only the inductive effect of CF_3 is involved. For example, $I(\text{CF}_3\text{CH}_2) - I(\text{CH}_3) = 0.76$ v.,

(16) A. G. Harrison, P. Kebarle, and F. P. Lossing, *ibid.*, 83, 777 (1961).

(17) J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *ibid.*, 84, 4 (1962).

(18) A. Streitwieser, Jr., in "Progress in Physical Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1963, p. 1.

(19) R. W. Taft, Jr., N. C. Deno, and P. S. Skell, *Ann. Rev. Phys. Chem.*, 9, 287 (1958).

(20) L. D. Isaacs, W. C. Price, and R. G. Ridley in "The Threshold of Space," M. Zelikoff, Ed., Pergamon Press Ltd., London, 1957, p. 143.

(21) G. Herzberg and J. Shoosmith, *Can. J. Phys.*, 34, 523 (1956).

(11) R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc. (London)*, A258, 459 (1960).

(12) W. C. Price, T. R. Passmore, and D. M. Roessler, *Discussions Faraday Soc.*, 35, 201 (1963).

(13) J. L. Margrave, *J. Chem. Phys.*, 31, 1432 (1959).

(14) J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, 33, 861 (1955).

(15) R. Taubert and F. P. Lossing, *J. Am. Chem. Soc.*, 84, 1523 (1962).

Table II. Values of $I(\text{CF}_2)$ and $\Delta H_f(\text{CF}_2)$

$I(\text{CF}_2)$, v.	$\Delta H_f(\text{CF}_2)$, kcal./mole	Method	Ref.
...	< -20	Hg-photosensitized decomposition of C_2F_4	<i>a</i>
...	< -18	E for $\text{Na} + \text{CF}_3$	<i>b</i>
...	-23	Bond lengths and frequencies	<i>c</i>
13.3	-5 ± 10	Direct ionization of CF_2	3
11 ± 1	-30 ± 20	$A(\text{CF}_2^+)$ from $\text{C}_2\text{F}_4 = 15.2$ v.	13
...	-35 ± 10	CF_2 in CF_4 -graphite reactions	<i>d</i>
...	-17	Appearance potentials	<i>e</i>
...	-46 ± 5	Thermochemistry	<i>f</i>
...	-17	Thermochemistry	<i>g</i>
...	-35 ± 10	Reinterpretation of ref. 26	<i>h</i>
...	< -36.8	$A(\text{CF}_2^+)$ from $\text{C}_2\text{F}_4 = 15.13$ v.	7
...	> -45	Predissociation in CF_2	<i>i</i>
...	~ -20	$\Delta H_f(\text{CF}_2^+) = 250-266$ kcal./mole	<i>j</i>
...	-35 to -50	Pyrolysis of CF_2ClH	<i>k</i>
~12.1	< -35	Appearance potentials	<i>l</i>
<12.4	-	$\Delta H_f(\text{CF}_2^+) < 240 \pm 10$ kcal./mole	<i>m</i>
11.7	~ -36	This work	..

^a B. Atkinson, *J. Chem. Soc.*, 2684 (1952). ^b J. F. Reed and B. S. Rabinovitch, *J. Phys. Chem.*, **61**, 598 (1957). ^c C. R. Patrick, *Tetrahedron*, No. 4, 26 (1958). ^d L. Brewer, J. L. Margrave, R. F. Porter, and K. Wieland, *J. Phys. Chem.*, **65**, 1913 (1961). ^e J. R. Majer and C. R. Patrick, *Nature*, **192**, 866 (1961). ^f "JANAF Thermochemical Tables," D. R. Stull, Ed., The Dow Chemical Co., Midland, Mich., 1961; quoted in ref. *h*. ^g R. M. Potocki and D. E. Mann, NBS Report No. 1439, U. S. Government Printing Office, Washington, D. C., Feb. 15, 1962. ^h J. L. Margrave, *Nature*, **197**, 376 (1963). ⁱ B. A. Thrush and J. J. Zwolenik, *Trans. Faraday Soc.*, **59**, 582 (1963). ^j D. L. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **68**, 575 (1964). ^k F. Gozzo and C. R. Patrick, *Nature*, **202**, 80 (1964). ^l J. R. Majer and C. R. Patrick, *ibid.*, **201**, 1022 (1964). ^m W. C. Steele, *J. Phys. Chem.*, **68**, 2359 (1964).

and $I(\text{CF}_3\text{CF}_2) - I(\text{HCF}_2) = 0.53$ v. For substitution on a benzene nucleus the effect is about the same: $I(\text{CF}_3\text{C}_6\text{H}_5) - I(\text{C}_6\text{H}_6) = 9.68 - 9.25 = 0.43$ v.²⁰ These comparisons suggest that the observed value of $I(\text{CF}_3\text{CH}_2)$ may be a little too high. It may be noted that, as expected, the substitution of CF_3 for F on a β -carbon, as shown by $I(\text{CF}_3\text{CF}_2)$ and $I(\text{CF}_3\text{CF}_2\text{CF}_2)$ in Table I, causes little change in ionization potential.

The observed order of the ionization potentials of the perfluoroalkyl radicals is of importance in accounting for the differences between the mass spectra of alkanes and of perfluoroalkanes. The order is inverted with respect to the ionization potentials of alkyl radicals.¹⁵ It has been pointed out,⁹ for instance, that in perfluoroalkanes the abundance of C_3F_7^+ ions is much greater in molecules containing a $n\text{-C}_3\text{F}_7$ group than in molecules containing only $i\text{-C}_3\text{F}_7$ groups, suggesting that the observed C_3F_7^+ ion is mainly $n\text{-C}_3\text{F}_7^+$. This is consistent with $I(n\text{-C}_3\text{F}_7) < I(i\text{-C}_3\text{F}_7)$ as found in this work. In the spectra of C_5 and C_6 perfluoroparaffins⁹ the low abundance of higher perfluoroalkyl ions compared to CF_3^+ abundance also suggests increasing ionization potential along the radical series.

CF_2 Radical and Ion. The decomposition of C_2F_5 radicals at $>950^\circ$ by a C-C bond rupture rather than by loss of an F atom is in contrast to the behavior of C_2H_5 radicals. It indicates a considerable stabilization of CF_2 compared to CH_2 . As can be seen from Table II, estimates for $\Delta H_f(\text{CF}_2)$ cover a wide range from -5 to -45 kcal./mole. The more recent estimates^{7,22,23} favor a value of -35 kcal./mole as an upper limit. A lower limit of -45 kcal./mole has been obtained.²⁴ Majer and Patrick concluded recently²⁵ from a study of CF_2^+ appearance potentials that the most probable values for CF_2 were $\Delta H_f(\text{CF}_2^+) \sim 240$ kcal./mole, $\Delta H_f(\text{CF}_2) < -35$ kcal./mole, and

hence $I(\text{CF}_2) \sim 12.1$ v. A similar conclusion has been reached by Steele.²⁶ The vertical ionization potential found in this work, 11.7 v., is in reasonable agreement with these estimates and is much lower than the earlier direct measurement of 13.3 v.³ Using the appearance potential of CF_2^+ from C_2F_4 , which appears to be reliably measured as 15.13 ± 0.1 v.,^{7,13} we obtain $D(\text{CF}_2=\text{CF}_2) \sim A(\text{CF}_2^+) - I_{\text{vert}}(\text{CF}_2) = 79$ kcal./mole, and $\Delta H_f(\text{CF}_2) \sim -36$ kcal./mole. Since either $A(\text{CF}_2^+)$ or $I_{\text{vert}}(\text{CF}_2)$, or both, may contain appreciable excess energy above the threshold for formation of CF_2^+ in its lowest vibrational level, the limits of error cannot be estimated. By comparison with $D(\text{CH}_2=\text{CH}_2)$ which appears to be in the range 148-160 kcal./mole,²⁷ $D(\text{CF}_2=\text{CF}_2) \sim 80$ kcal./mole is a remarkably weak double bond, illustrating the great stability of the CF_2 radical.^{13,22,28}

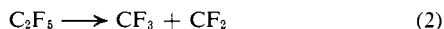
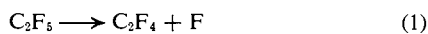
By analogy with the effect of F atoms on the stabilization of CH_2F^+ , CHF_2^+ , and CF_3^+ ions, one would expect $I(\text{CF}_2)$ to be lower than $I(\text{CH}_2)$ (10.396 v.²⁹) and would conclude that the present value of 11.7 v. refers to formation of an excited CF_2^+ ion in the vertical process. On the other hand, the greatly enhanced stability of the neutral CF_2 over that of the neutral CH_2 may result in the ionization potential of CF_2 being the larger. Support for this value of $I_{\text{vert}}(\text{CF}_2)$ has recently been reported. Pottie found 11.86 v. by a direct electron impact measurement,³⁰ and McGee and Martin³¹ report a value of 11.8 v. measured on CF_2 radicals produced in the pyrolysis of CF_3I , using an R.P.D. ion source.

Thermal Dissociation of C_2F_5 Radical. The thermal dissociation of the C_2F_5 radical by C-C bond scission

(22) See ref. *h*, Table II.
 (23) See ref. *k*, Table II.
 (24) See ref. *i*, Table II.
 (25) See ref. *l*, Table II.

(26) See ref. *m*, Table II.
 (27) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).
 (28) See ref. *c*, Table II.
 (29) G. Herzberg, *Can. J. Phys.*, **39**, 1511 (1961).
 (30) R. F. Pottie, reported at the A.S.T.M. Committee E-14 Meeting, Montreal, June 1964.
 (31) H. A. McGee and W. J. Martin, *J. Am. Chem. Soc.*, in press.

rather than by loss of an F atom, although surprising at first sight, is consistent with the bond dissociation energies concerned. For the reactions



$D(\text{C}_2\text{F}_4-\text{F}) = \Delta H_f(\text{C}_2\text{F}_4) + \Delta H_f(\text{F}) - \Delta H_f(\text{C}_2\text{F}_5)$ and $D(\text{CF}_3-\text{CF}_2) = \Delta H_f(\text{CF}_3) + \Delta H_f(\text{CF}_2) - \Delta H_f(\text{C}_2\text{F}_5)$. Subtracting, $D(\text{C}_2\text{F}_4-\text{F}) - D(\text{CF}_3-\text{CF}_2) = \Delta H_f(\text{C}_2\text{F}_4) + \Delta H_f(\text{F}) - \Delta H_f(\text{CF}_3) - \Delta H_f(\text{CF}_2)$. Taking the best estimates,⁸ $\Delta H_f(\text{C}_2\text{F}_4) = -152$, $\Delta H_f(\text{F}) = +18.9$, $\Delta H_f(\text{CF}_3) = -115 \pm 5$, and $\Delta H_f(\text{CF}_2) = -35$ kcal./mole, $D(\text{C}_2\text{F}_4-\text{F})$ is greater than $D(\text{CF}_3-\text{CF}_2)$ by ~ 17 kcal./mole. A rather large error in $\Delta H_f(\text{CF}_3)$ or $\Delta H_f(\text{CF}_2)$ or a large difference in the activation energies

E_{-1} and E_{-2} for the reverse reactions would be needed to make reaction 1 competitive.

Appearance Potential Curves for C_2F_5^+ . The appearance potential curves for C_2F_5^+ fragment ions were obtained from C_3F_8 , $\text{C}_2\text{F}_5\text{H}$, C_3F_8 , and C_4F_{10} . For these compounds the C_2F_5^+ ion curves showed considerable tailing and no reliable evaluation of the threshold for C_2F_5^+ formation could be made using the present technique.

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A Pulse Radiolysis Study of Peroxy Radical-Aromatic Amine Reactions

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Pulse radiolysis is used to produce peroxy radicals under conditions that allow the mode and rate of their interaction with aromatic amines to be observed directly. Cyclohexyl peroxy radicals in cyclohexane form complexes with diphenylamine (DA) and N-methylaniline, while no complex is observed with N,N'-diphenyl-p-phenylenediamine (N,N'-DPPD) under the same conditions. Deuterium isotope effects are observed and used to interpret the results. α -Ethanol peroxy radicals in ethanol form long-lived complexes with all aromatic amines tested. Implications of these results to the basic mechanism of oxidation inhibition are discussed.

Introduction

Application of the technique of pulse radiolysis to the study of peroxy radicals¹ offers a unique opportunity to test some of the mechanisms proposed for inhibition of oxidation.^{2,3} Previously, we had demonstrated that pulse radiolysis of cyclohexane containing dissolved oxygen produced high concentrations of cyclohexyl peroxy radicals and that their rate of disappearance could be followed spectroscopically. Cyclohexyl peroxy radicals produced in the concentration range of $>10^{-4}$ M, decayed by second-order kinetics to produce cyclohexanone and cyclohexanol in equal quantities. The half-life under these conditions is a few milli-

seconds ($k_0 = 2 \times 10^6$ l./mole) and corresponds to a disproportionation reaction retarded by a high steric factor. Cyclohexyl peroxy radicals absorb in the region of 2900 Å. Since most inhibitors (aromatic amines were used for this study) absorb strongly in this region, it is necessary to observe either the rate of elimination of inhibitor or the rate of formation of one of the reaction products. This paper presents direct spectroscopic evidence for the mechanism of amine-peroxy radical reactions and reports a method for obtaining absolute rate constants for the antioxidation process.

Experimental

Pulse Radiolysis Apparatus. The pulse radiolysis setup used for these experiments is shown schematically in Figure 1. A single 5- μ sec. electron pulse is supplied by a Varian linear accelerator. Energy is nominally 8 Mev. with a beam current of 150 to 200 ma. Solutions in the radiolysis cell were changed after each electron pulse, using the reservoir flushing system shown also in Figure 1. Prior to filling the cell, oxygen was bubbled through the solutions for 5 min., and then the center movable dip tube was forced below the solution surface thus pumping the liquid into the cell. A constant pressure of oxygen was then used to drive fresh solution into the cell by operation of a solenoid valve on the exhaust side. Deoxygenated solutions were prepared by flushing with Airco 99.99% argon for 30 min. before cell filling.

Reagents. Cyclohexane was Eastman Spectrograde used without further purification. Ethanol was Pharmco U.S.P. absolute; 2-propanol and methanol

(1) (a) R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.*, **57**, 1107 (1961); (b) R. L. McCarthy and A. MacLachlan, *J. Chem. Phys.*, **35**, 1625 (1961).

(2) For a review, see K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).

(3) (a) G. S. Hammond, C. E. Boozer, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3238 (1955); (b) C. E. Boozer and G. S. Hammond, *ibid.*, **76**, 3861 (1954); (c) C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *ibid.*, **77**, 3233 (1955).