exchange is measured. A decrease in ethyl iodine concentration also decreases the apparent rate and at low ethyl iodide concentrations no exchange will be observed. The low velocity constant also requires a relatively long time to accurately study this process. A run at 10^{-3} M I_2 and with no solvent will show a fraction of a per cent exchange per day and at approximately 3×10^{-3} M will not be statistically observable.

Comparison with Other Work. This study has shown that there is a significant thermal exchange of ethyl iodide and iodine at room temperature. This fact can help explain some of the anomalies in other studies on the ethyl iodide–iodine system. In the study of the radiation chemistry of alkyl iodide and iodine, Hanrahan and Willard[11] were able to predict theoretically the yields of iodine, hydrogen iodide, and the rate of induced exchange. They found that all of their predictions were in agreement with their experimental data except for the rate of induced exchange. The experimental values were higher by a constant increment of 0.020 μequiv./min. The reason for this discrepancy was not clear and was attributed to "hot" processes involving ethyl iodide molecules with too little energy to produce radicals. The thermal exchange measured in this study had a value of 0.017 μequiv./min., which is in excellent agreement.

Darbee and Harris[7] have studied this system at conditions close to those of this study and could not obtain reproducible data. At 10^{-2} M iodine they obtained a rate law of $R = k(I_2)$ and attributed the exchange to a complex formation. Their irreproducibility at 10^{-3}–10^{-4} was probably due to the factors discussed previously. At 10^{-2} M the iodine independent mechanism would not be seen.

Behrens and Maddock[18–20] have reported work on the methyl iodide–iodine system at 35°. They indicated the exchange follows a rate law of $R = k(I_2)^{-1}$. In later work Behrens[20] indicated that the exchange was subjected to a heterogeneous contribution, but in the earlier work Behrens and Maddock[18] indicated that under identical conditions their data had not been satisfactorily reproduced. In addition, samples in the same set of vessels with and without glass packing gave similar results. In relation to this work the methyl iodide exchange is faster than that of ethyl iodide at 35°, 7.55 $\times$ 10^{-6} *vs.* 2.55 $\times$ 10^{-6} M/hr. However, considering the observed irreproducibility in these systems, the agreement is good. There was no indication of a radiation intensity effect in this system and no heterogeneous contribution. This might indicate that methyl iodide has a different exchange mechanism. This was further confirmed by the 8.4-kcal. activation energy for methyl iodide which is considerably lower than the value reported here for ethyl iodide.

Szilard–Chalmers Effect. The data indicate that there is a rapid apparent exchange between ethyl iodide and iodine at low concentrations. This would help to explain some of the inconsistencies in the hot-atom work on ethyl iodide systems.[47]

Acknowledgment. The authors wish to thank Dr. Harold Kwart for many stimulating discussions regarding the mechanism of this reaction.

(47) The possible implications of this work on the Szilard–Chalmers effect are to be discussed elsewhere.

Effects of Resonance and Structure on the Thermochemistry of Organic Peroxy Radicals and the Kinetics of Combustion Reactions[1]

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Recent data on the H-bond dissociation energy in $H–O_2$ and the reasonable assumption that $D°(RO_2–H) = D°(HO_2–H)$, together with $\Delta H_f°$ for the peroxides, permit the evaluation of the bond dissociation energies $D°(R–O_2 \cdot)$ and $D°(RO_2–R)$ for a number of different groups R. Using estimated entropies for radicals and molecules, it is possible to estimate equilibrium constants and ceiling temperatures for the reaction $R \cdot + O_2 \rightleftarrows RO_2 \cdot$. These temperatures are quite high for $R = H$ or alkyl radicals, but rather low for $R =$ allyl or benzyl. They do indicate that $RO_2 \cdot$ will be important in cool flame reactions. Using similar data, other reactions of $RO_2 \cdot$ radicals are discussed. Additions to olefins are shown to have low ceiling temperatures but not the additions to dienes or styrene. Internal abstraction of $RO_2 \cdot$ and four-center reactions of $R \cdot + O_2$ are shown to be probably unimportant. Termination reactions involving $RO_2 \cdot$ are shown to be likely only for $RO \cdot$ (disproportionation) and $R \cdot$ (addition and disproportionation). In solution the reaction $2RO_2 \cdot \rightarrow 2RO \cdot + O_2$, which is a propagation reaction, can also lead to a small but important amount of cage recombination of $2RO$. It is shown that above 150° the distribution of primary products in hydrocarbon oxidation is given by the expression

$$d(RO_2H)/d(olefin) = K_{eq}k_a(RH)/k_1'$$

where K_{eq} is the equilibrium constant for the reaction $R \cdot + O_2 \rightleftarrows RO_2 \cdot$, k_a is the rate constant for $RO_2 \cdot + RH \rightarrow RO_2H + R \cdot$, and k_1' is for $R \cdot + O_2 \rightarrow HO_2 \cdot + olefin$.

Introduction

There seems to be a fairly general agreement that the degradative oxidation of organic molecules RH proceeds by a radical mechanism in which a hydrogen atom is abstracted and the $R \cdot$ radical produced then reacts with O_2 molecules. At low temperatures (e.g., $<250°$) this latter reaction appears to be an association leading to the formation of peroxy radicals, $RO_2 \cdot$. At higher temperatures, a further hydrogen atom abstraction by O_2 becomes increasingly important leading to olefin and $HO_2 \cdot$ production. This dual path may be represented by[2a]
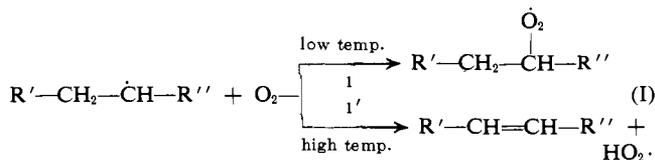
The low temperature path leads to the formation of peroxides and hydroperoxides together with their decomposition products, while the high temperature path leads to olefin formation plus H_2O_2 and H_2O.[2b]

Despite a great deal of work on the kinetics and the products of oxidations, very little effort has been spent on exploring the thermochemistry of the peroxy radicals. Within the past few years bond energy data and additivity rules have been developed which make possible the estimation of heats of formation and entropies of these radicals with reasonable precision. It is the purpose of the present paper to adapt these data to peroxy radicals having varying organic structures so as to explore the thermochemistry and kinetics of reaction 1 and their bearing on the kinetics of subsequent steps in the oxidation of organic molecules.

Thermochemistry of $RO_2 \cdot$ Radicals

The only reliable data on O–H bond energies in hydroperoxides is that for H_2O_2 itself. Mass spectrometric data of Foner and Hudson[3] have yielded a value of $D°(H-O_2) = 47 \pm 2$ kcal. Using this value and the standard heats of formation of $H_2O_2(g)$,[4] $\Delta H_f°(H_2O_2) = -32.5$ kcal., and $\Delta H_f°(H) = 52.1$ kcal. we find $D°(HO_2-H) = 90 \pm 2$ kcal.

To proceed we need to know the value of $D°(RO_2-H)$. There is no direct measurement of this bond strength, but it is reasonable to assume that it would be very close to the value of $D°(HO_2-H)$.[5] This would correspond to the bulk of observations on bond dissocia-

(2) (a) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. E. Vaughan, *Discussions Faraday Soc.*, 10, 242 (1951); (b) J. H. Knox and C. H. J. Wells, *Trans. Faraday Soc.*, 59, 2786 (1963).

(3) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, 36, 2681 (1962).

(4) Unless otherwise indicated, all thermodynamic data are taken from the JANAF Interim Thermochemical Tables (issued from the Thermal Laboratory of the Dow Chemical Co., Midland, Mich., 1960–1964), or else the A.P.I. Tables, Research Project No. 44, Carnegie Press, Pittsburgh, Pa., 1953. Standard states are taken to be hypothetical ideal gas at 25° and 1 atm. pressure.

(5) This conclusion is supported by two independent bodies of evidence. From kinetic data on the rate of oxidation of i-C_4H_{10} to t-BuO$_2$H,[2a] it is possible to deduce that $D°(t$-BuO$_2$-H) must be reasonably close to $D°(t$-Bu–H); otherwise, the reaction would not occur. This places the value in the vicinity of 91.5 kcal. [H. Teranishi and S. W. Benson, *J. Am. Chem. Soc.*, 85, 2887 (1964)]. If the value were even 4 kcal. lower (i.e., 87.5 kcal.) it can be shown that the yield of RO_2H would tend to be very small. Other kinetic data of Dr. J. R. Thomas (unpublished) on the very rapid rate of reaction of $C_6H_5O \cdot$ radicals with RO_2H places the value of $D°(RO_2-H)$ in the vicinity of $D°(C_6H_5O-H)$ which is about 88 kcal. A value of 92 kcal. would make the reaction extremely slow.

tion energies which indicate that while neighboring groups may have large effects of up to ± 15 kcal. on bond strengths, next-neighboring groups are expected to have very little effect. On this basis we shall assign $D°(RO_2-H) = D°(HO_2-H) = 90 \pm 2$ kcal. Further support for such a conclusion comes from the observations that in the isoelectronic sequences, $D°(RCH_2-CH_2-H)$, $D°(RCH_2O-H)$, $D°(RCH_2NH-H)$, and $D°(RNHNH-H)$, the replacement of R by H does not appear to affect the value of the bond strength.[6]

A recent compilation of thermodynamic data on the peroxides and hydroperoxides by the author[7] has shown that they obey reasonably well the scheme of additivity of group values.[8] This also seems to be the case for a few recently studied peroxy acids and esters.[9]

This makes possible the calculation of $\Delta H_f°(RO_2 \cdot)$[10] and where data are known for $\Delta H_f°(R \cdot)$ it is possible to compute the bond strengths, $D°(R-O_2 \cdot)$. Table I contains a list of values for a number of different R groups of interest. It can be seen that for the saturated radicals $R \cdot$, the bond strengths are all in the neighborhood of 28 kcal., while conjugatively stabilized radicals such as allyl or benzyl have bond energies weakened by the amount of this resonance energy. An estimate of errors from all sources indicates that the tabulated $D°(R-O_2 \cdot)$ have expected uncertainties of ± 2.5 kcal.

Table I. Standard Heats of Formation for $R \cdot$ and $RO_2 \cdot$ Radicals in the Gas Phase and Standard Heats of Dissociation, $D°(R-O_2 \cdot)$[a]

Group R	$\Delta H_f°(R \cdot)$	$\Delta H_f°(RO_2 \cdot)$	$D°(R-O_2 \cdot)$[b]
H	52	5	47
CH_3	32	6	26
C_2H_5	26	−2	28
i-C_3H_7	17.6[c]	−11	29
t-C_4H_9	6.7[d]	−21	28
$CH_2=CHCH_2$	38[e]	23[g]	15
$C_6H_5CH_2$	44[f]	31[h]	13

[a] All values are in kcal./mole for standard states of 1 atm., 25°. [b] $D°(R-O_2 \cdot)$ is the standard enthalpy change for the reaction $RO_2 \cdot \rightleftharpoons R \cdot + O_2$. [c] P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, 86, 2770 (1964). [d] H. Teranishi and S. W. Benson, *ibid.*, 85, 2887 (1963). [e] Based on allyl resonance energy of 13 kcal. and a primary C–H bond strength in propane of 98 kcal.: P. S. Nangia, A. N. Bose, and S. W. Benson, *ibid.*, 85, 1388 (1963); D. Golden, K. Egger, and S. W. Benson, *ibid.*, 86, 5420 (1964). [f] R. K. Boyd, G. W. Downs, J. S. Gow, and C. Horrex, *J. Phys. Chem.*, 67, 719 (1963); G. L. Esteban, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3873 (1963); J. H. Buss and S. W. Benson, *J. Phys. Chem.*, 61, 104 (1957). [g] Value based on an estimate of −31 kcal. for $\Delta H_f°$ of allyl alcohol. This assumes no important interaction of the OH and double bond; i.e., the heat of hydrogenation of allyl alcohol is the same as propylene. That such interactions are small is indicated by the fact that propylene and acrylic acid have the same heats of hydrogenation: C. T. Mortimer, "Reaction Heats and Bond Strengths," Addison-Wesley Publishing Co., Reading, Mass., 1962, p. 52. [h] Value based on $\Delta H_f°(C_6H_5CH_2OH(g)) = -23.2$ mole taken from the value for liquid measured by G. S. Parks, K. E. Manchester, and L. M. Vaughan, *J. Chem. Phys.*, 22, 2089 (1954), and estimates of ΔH_{vap} from vapor pressure data. These also yield $\Delta H_f°(C_6H_5CH_2OOH(g)) = -7$ kcal./mole.

(6) P. Grey and A. Williams, *Chem. Rev.*, 59, 239 (1959); A. F. Trotman-Dickenson, *et al.*, *J. Chem. Soc.*, 3217, 3879 (1963).

(7) S. W. Benson, *J. Chem. Phys.*, 40, 1007 (1964).

(8) S. W. Benson and J. H. Buss, *ibid.*, 29, 546 (1958).

(9) H. A. Swain, Jr., L. S. Silbert, and J. G. Miller, *J. Am. Chem. Soc.*, 86, 2562 (1964). Although the authors have not made the comparisons from their group values for the peracids, it is possible to compute $\Delta H_f°$ (esters) in good agreement (± 2 kcal.) with their own measured values. This indicates that there are negligibly weak intramolecular H bonds in the acids.

(10) S. W. Benson, *ibid.*, 86, 3922 (1964).

In Table II are listed the standard molar entropies and heat capacities at 25°, for the same radicals R· and RO₂· in the gas phase. Values for H and CH₃

Table II. Estimated Standard Entropies and Molar Heat Capacities of R· and RO₂· Radicals in the Gas Phase[a]

Group R	$S°$ (R·)	$S°$ (RO₂·)	$-\Delta S_1°$	$C_p°$ (R·)	$C_p°$ (RO₂·)	$-\Delta C_p°_1$
H	27.4	58.0	18.4	5.0	10.3	1.7
CH₃	46.2	64.6	30.6	8.5	14.2	1.3
C₂H₅	57.1	74.1	32.0	12.6	18.7	0.9
i-C₃H₇	66.0	82.5	32.5	17.6	26.8	2.2
t-C₄H₉	71.0	85.9[b]	34.1	23.1	30.4	−0.3
CH₂=CHCH₂	61.7	83.7	27.0	14.3	25.2	−3.9
C₆H₅CH₂	77.0	96.0	30.0	23.5	34.8	−4.3

[a] All values in cal./mole °K. for hypothetical ideal gas at 1 atm., 25°. [b] Estimated from group additivity values listed in ref. 11 together with the recent group value $S°[C(O)(C)_3–C(O)(H)_3]$ = −64.0 cal./mole. °K., taken from F. L. Oetting, *J. Phys. Chem.*, 67, 2757 (1963). The model compound *t*-BuCH=CH₂ yields an entropy abnormally low by 2.5 e.u. which makes the API listed value for this compound suspect.

are taken from the JANAF tables,[4] while all the others have been estimated by the author. The values of $C_p°$ for the radicals R· have been estimated by taking it as the same as that of the corresponding alkane RH. For RO₂·, the values of $C_p°$ have been estimated to correspond to that of the structurally similar olefin RCH=CH₂. At 25° this should be an excellent estimate. At higher temperatures it would be a somewhat high estimate. Where better precision is required at the higher temperatures, $C_p°$ for the RO₂ can be taken as $C_p°(RCH=CH_2)$ minus the contributions of three C–H stretching vibrations of about 3000 cm.⁻¹ each and six C–H bending vibrations of about 1200 cm.⁻¹ each. Only these latter should be appreciable.

Entropies for the R· radicals were assigned by starting with the entropy of the nearest RH molecule and making appropriate corrections for symmetry and electron spin ($R \ln 2$). For these purposes the geometry of the R· radical is taken as planar. The entropies of RO₂· were similarly estimated by taking as starting point the molecular analog RCH=CH₂, and adding $R \ln 2$ for spin. Thus for CH₃OO, the model compound is CH₃CH=CH₂ with $S°$ = 63.9. For further comparison, the even closer model CH₃CHO has $S°$ = 63.2. Alternatively, it is possible to estimate the entropy of the parent hydroperoxides from the group additivity relations given by the author[11] and then correct these for spin ($+R \ln 2$), symmetry ($−R \ln \sigma$), and one internal rotation (O–O–H) of about 2.5 cal./mole.°K. For CH₃OO this procedure yields the value of 65.2 cal./mole. °K. in excellent agreement with the value of 64.6 listed in Table II.

It is interesting to note that, except for R = H or allyl (C₃H₅), the values of $\Delta S°$ fall very close to −32 cal./mole °K. The low value for R = allyl is a consequence of the rigid structure and symmetry of the allyl radical. The loss of a hindered rotation amounts to about 2 cal./mole °K. The uncertainty in the values of $\Delta S(RO_2·)$ are estimated at about ±1.5 cal./mole °K. at 25°.

(11) S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1960, Appendix D.

In Table III are listed the values of K_{eq} for reaction 1 at 300, 500, and 700°K. For all temperatures we that K_{eq} is extremely large for R = H so that one

Table III. Estimated Values of K_{eq} for the Gas Phase Association R· + O₂ ⇌ RO₂· at 300, 500, and 700°K.

Group R	Log K_{eq}, atm.⁻¹ 300°K.	500°K.	700°K.
H	30.4	16.4	10.6
CH₃	12.3	4.6	1.35
C₂H₅	13.5	5.2	1.50
i-C₃H₇	14.1	5.5	1.85
t-C₄H₉	13.0	4.6	0.97
CH₂=CHCH₂	5.0	0.75	− 0.97
C₆H₅CH₂	2.92	− 1.0	− 2.2

expects HO₂· to be an important radical in kinetic systems at these temperatures if H atoms are present (*e.g.*, H₂ + O₂ reaction). For the saturated alkyl radicals, K_{eq} has about the same value at each temperature and does not appear to be very sensitive to structure. At 300 and 500°K., K_{eq} is sufficiently large that one would expect to find RO₂· very large relative to R·, even at quite low O₂ pressures. However, at 700°K. this is no longer the case and the equilibrium will now be very sensitive to the partial pressure of O₂.

An extreme case is represented by the unsaturated, resonance-stabilized radicals, C₃H₅· and C₆H₅CH₂·. Here K_{eq} is already quite unfavorable at 500°K. Combining the uncertainties in ΔH and ΔS, it is estimated that the uncertainty in ΔF is ±2.7 kcal. over the temperature range. This introduces an error in log K_{eq} of about ±2 log units at 300°K., ±1.2 units at 500°K., and ±0.9 unit as 700°K. In the most important range of 500–700°K., the error in K_{eq} can be a power of 10.

A simpler measure of the extent of equilibrium in these systems is given by what may be termed the "ceiling temperature." In terms of equilibrium concentrations ,we can express the conversion of R· to RO₂· by

$$\frac{(RO_2·)_{eq}}{(R·)_{eq}} = K_{eq}(O_2) \qquad (II)$$

If now we select a standard pressure of O₂, we then can define the ceiling temperature at which the ratio $(RO_2·)/(R·)$ = 1. This is given from the free energy relation, $\Delta F = −RT \ln K_{eq}$ as the temperature at which $\Delta H = T\Delta S$. In Table IV are shown some approximate ceiling temperatures for reaction I for different partial pressures of O₂.

Table IV. Approximate Ceiling Temperature for the Gas Phase Equilibrium R· + O₂ ⇌ RO₂· at Different Partial Pressures of O₂

Group R	Ceiling temp., °C. Partial pressure of O₂, atm. 1	0.1	0.01	0.001
H	2000	1650	1350	1150
CH₃	560	470	380	300
C₂H₅	590	490	400	340
i-C₃H₇	600	500	410	350
t-C₄H₉	520	420	350	290
CH₂=CHCH₂	300	200	140	90
C₆H₅CH₂	160	100	60	25

It may be seen that the ceiling temperature is very sensitive to O_2 pressures, the ceiling temperature dropping by roughly 90° for each power of 10 by which P_{O_2} decreases except at very low temperatures. The radicals form three distinct groups. $HO_2 \cdot$ has the highest ceiling temperatures at all pressures, well in in excess of 1000°. The saturated radicals $RO_2 \cdot$ have ceiling temperatures which vary from about 330° at the lowest P_{O_2} (~1 mm.) to about 550° at $P_{O_2} = 1$ atm. The former temperatures would correspond to about the cool flame regions, while the latter would be slightly above the normal fast oxidation and explosion regimes. Finally for the stabilized radicals we see that ceiling temperatures are only about 100° above room temperatures. The expected uncertainties in these ceiling temperatures is about ±50° and may be ±75° at temperatures near 700°.

The significance of these ceiling temperatures is that for the given O_2 pressure they tell us approximately the temperature at which the equilibrium concentrations of $RO_2 \cdot$ and $R \cdot$ radicals would be expected to be equal. At much higher O_2 pressures, but fixed temperature, $(RO_2 \cdot)_{eq} \gg (R \cdot)_{eq}$, while at fixed P_{O_2}, but higher temperatures, $(RO_2 \cdot)_{eq} \ll (R \cdot)_{eq}$. How different these equilibrium concentrations would be from ambient steady-state concentrations would depend on the relative rates of competing reactions of both $R \cdot$ and $RO_2 \cdot$, relative to reaction 1 and its reverse. Since $R \cdot + O_2$ addition is a very fast bimolecular reaction[12] compared to competing reactions of $R \cdot$ such as H abstraction or addition to olefins,[13a] while decomposition of $RO_2 \cdot$ at ceiling temperatures or higher is expected to be a fast unimolecular process compared to H abstraction, the deviations from thermodynamic concentrations is not expected to be great.

This is, however, subject to considerations of the kinetic importance of third bodies in quenching the nascent, vibrationally excited $(RO_2 \cdot)^*$. It is not unlikely that the lifetimes for such species may be of the order of 10^{-8} to 10^{-9} sec. at 400°[13b] which would make redissociation quite probable at pressures of the order of 100 mm. This would be a reasonable explanation for the increasing importance of olefin formation at higher temperatures (>350°), a tendency not easily explainable by the high ceiling temperatures shown in Table IV (column 3, $O_2 = 0.1$ atm.).

(12) D. P. Dingledy and J. G. Calvert, *J. Am. Chem. Soc.*, **85**, 856 (1963); J. G. Calvert and W. C. Sleppy, *ibid.*, **81**, 769 (1959).

(13) (a) J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," Vol. I, Pergamon Press, Oxford, England, 1961, Chapter 4. (b) The rate constant for the addition of $R \cdot$ to O_2 is about $10^{9.6}$ l./mole sec. at 25° (ref. 12) for $R \cdot = CH_3 \cdot$ or $Et \cdot$. The competing reaction to form $HO_2 \cdot$ + olefin is at least 10^3 slower under the same conditions indicating an activation energy of about 4 kcal. together with an A factor of 10^9 l./mole sec. There is no way in which the olefin rate constant could ever exceed the addition rate constant at 400° except by third body restrictions. That the quoted lifetimes are reasonable is indicated by the fact that $CH_3 \cdot + O_2$ recombination appears to be third order[12] at 25°. (c) H. D. Medley and S. D. Cooley, *Advan. Petrol. Chem. Refining*, **3**, 309 (1960), particularly pp. 319–323. (d) C. N. Satterfield and R. C. Reid, *J. Phys. Chem.*, **59**, 283 (1955). (e) G. Dixon-Lewis and A. Williams, *Nature*, **196**, 1309 (1962); C. P. Fenimore and G. W. Jones, Preprints, Tenth International Symposium on Combustion, Cambridge, England, Aug. 1964. From the data in these papers, it would appear that the chemiluminescence from excited OH^* observed during the induction period behind incident shocks in $O_2 + H_2$ mixtures [F. E. Belles and M. Lauver, *J. Chem. Phys.*, **40**, 415 (1964)] can be well accounted for by the exothermic bimolecular reaction: $O + HO_2 \rightarrow HO + O_2 + 54$ kcal. The extra 35 kcal. of activation needed to produce the ground state of excited OH^* still gives quite adequate rates of production of HO^*.

While there are no direct quantitative tests of the values for K_{eq} given for the ceiling temperatures listed, they are in agreement with a large body of qualitative evidence. Thus Knox and Wells[2b] have shown that in C_2H_6 gas phase oxidation, there is a turnover from CH_3OH, and CH_2O as major products at 314° to C_2H_4 at 364°. For the pressures of O_2 used this is within the limits of error cited for the ceiling temperatures from Table IV (400°). The butanes (Knox, private communication) follow similar behavior.

However let us note that it is not necessary to be above the ceiling temperatures in order for product turnover to occur. One must inquire further into the irreversible steps for the radicals produced in reactions 1 and 1′. If we accept that $RO_2 \cdot$ (from 1) and $HO_2 \cdot$ (from 1′) both disappear by irreversible abstraction reactions, then the product determining paths are

$$R \cdot + O_2 \underset{-1}{\overset{1}{\rightleftharpoons}} RO_2 \cdot$$

$$\overset{1'}{\longrightarrow} \text{olefin} + HO_2 \cdot$$

(A)

$$RO_2 \cdot + RH \overset{a}{\longrightarrow} RO_2H + R \cdot$$

$$HO_2 \cdot + RH \overset{a'}{\longrightarrow} HO_2H + R \cdot$$

If we neglect, as a first approximation, other sources of olefin and RO_2H and their secondary destruction, then the ratio of rates of formation of oxygen containing species to olefin in the steady state is

$$\frac{d(RO_2H)}{d(\text{olefin})} = \frac{k_a(RH)(RO_2 \cdot)}{k_1'(O_2)(R \cdot)}$$

(B)

and assuming long chains the steady-state $(RO_2 \cdot)/(R \cdot)$ ratio is

$$\frac{(RO_2 \cdot)}{(R \cdot)} = \frac{k_1(O_2)}{k_{-1} + k_a(RH)}$$

(C)

and on substitution we find

$$\frac{d(RO_2H)}{d(\text{olefin})} = \frac{k_1 k_a(RH)}{k_1'[k_{-1} + k_a(RH)]} \xrightarrow{[T > 200°]}$$

$$\frac{k_1 k_a(RH)}{k_1' k_{-1}} = \frac{K_{eq} k_a(RH)}{k_1'}$$

(D)

$$\xrightarrow[k_{-1} \ll k_a(RH)]{\text{low } T} \frac{k_1}{k_1'} \gg 1$$

(E)

$$\xrightarrow[k_{-1} \gg k_a(RH)]{\text{high } T} \frac{k_1}{k_1'} \left(\frac{k_a(RH)}{k_{-1}}\right) \leq 1$$

(F)

where $K_{eq} = k_1/k_{-1}$.

Thus the product turnover is decided not so much by the closeness to ceiling temperatures as by the relative rates of the dissociation step -1 and the competing slow bimolecular abstraction step a. Since k_a is expected to have Arrhenius parameters $A_a \sim 10^{8.5}$ l./mole-sec., $E_a \sim 14$ kcal. while $A_{-1} \sim 10^{14}$ sec.$^{-1}$ and $E_{-1} \sim 29$ kcal., the ratio $k_a(RH)/k_{-1}$ at $(RH) = 0.1$ atm. will be 3 at 100°; $10^{-1.6}$ at 500°K.; $10^{-2.2}$ at 550°K.; $10^{-2.8}$ at 600°K.; and $10^{-3.1}$ at 650°K. We see that even if $k_1/k_1' = 1000$ at 500°K., $d(RO_2H)/d(\text{olefin})$ will shift from 2.5 at 500°K. to about 0.4 at 650°K. even though the latter is still 100° below the ceiling temperature at $O_2 = 0.1$ atm. In actual practice since we expect the ratio k_1/k_1' to have a small

negative temperature coefficient this effect will become enhanced.

There are a considerable body of data supporting this interpretation of the product-determining steps in hydrocarbon oxidation.[13c] In their review of hydrocarbon oxidation Medley and Cooley present a number of tables of data on butane, propane, and ethane oxidation, all showing that at high temperatures where olefins are major products, an increase in total pressure from 1 to 10 atm. will reduce olefins to negligible yields in accord with eq. D.

Perhaps the most convincing data come from the survey of Satterfield and Reid,[13c] who showed that for C_3H_8 oxidation at about 1 atm., the results from twelve different laboratories, covering a temperature range of over 200° could be fitted roughly by

$$\log \left[\frac{d(\text{oxygen products})}{d(C_3H_6)} \right] =$$
$$-6.6 \ (\pm 0.5) + 19 \ (\pm 1.5)/\theta$$

where $\theta = 2.303RT$ in kcal./mole.

They mistakenly assigned this Arrhenius plot to the $\log (k_1/k_1')$ and were forced to draw some absurd conclusions about the Arrhenius parameters of step 1 as well as a ridiculously large activation energy for $1'$. However, we see from eq. D that this is really equal to $\log (K_{eq}k_a(RH)/k_1')$. Using the thermodynamic data from Tables I and II for K_{eq}, setting (RH) $\sim$ 1 atm., employing the Arrhenius parameters already cited for k_a, and setting $k_1 = 10^{8.5} - 3/\theta$ l./mole-sec. we estimate

$$\log (K_{eq}k_a(RH)/k_1') = -7.0 + 18.0/\theta$$

in excellent agreement with the propane data.

The importance of HO_2 at high temperatures is now fairly well documented by recent papers on flame studies[13e] in the temperature range 1200–2000°K. We can estimate from Table IV that the ceiling temperatures in solution for styryl peroxy-type radicals would be about 60° at about 1 torr O_2 ($\sim 3 \times 10^{-5} M$). The existence of such a ceiling temperature in the copolymerization of O_2 and either styrene or α-methylstyrene[14] at low O_2 concentrations is obscured by the competing reaction of $RO_2\cdot$ radical with monomer M to form $RO_2M\cdot$. This cuts down the apparent effect of the back reaction which would otherwise lead to an excess rate of styrene uptake relative to oxygen at the lowest O_2 pressures.

The low ceiling temperatures for the peroxides of the resonance-stabilized radicals shown in Table IV offers a reasonable explanation for the great difficulty in obtaining good yields of their hydroperoxides from sensitized autoxidations at temperatures above 100°.[15]

Above the ceiling temperatures reaction 1^{2a} would lead to production of dienes from allyl-type radicals, and quinoids from xylyl radicals. It is not clear what will happen to benzyl radicals above the ceiling temperatures.

Addition Reactions of $RO_2\cdot$ and $D(RO_2-R)$

While the ceiling temperatures offer a guide to a qualitative understanding of hydrocarbon oxidations

(14) A. A. Miller and F. R. Mayo, *J. Am. Chem. Soc.*, **78**, 1017 (1956).
(15) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 408. The system is, however, sufficiently complex that other causes may operate as well.

they cannot provide more than that since the course of these reactions depends as much or more on the relative rates of radical reactions as it does on radical concentrations. We can classify the reactions of $RO_2\cdot$ radicals in three categories: (a) H-atom abstraction (intra- and intermolecular) from molecules, (b) addition to unsaturated molecules, and (c) reactions with other radicals. Let us consider first the addition reactions to olefins.

From the $\Delta H_f°(RO_2\cdot)$ in Table I and the $\Delta H_f°$ (RO_2R) available in the literature,[7] it is possible to calculate the bond dissociation energies $D°(RO_2-R)$. These vary from 70 kcal. for $D°(CH_3O_2-CH_3)$ to 72 kcal. for $D°(EtO_2-Et)$ and 71 kcal. for $D°(t-BuO_2-t-Bu)$. There is not much error in choosing 71 ± 2 kcal. as a mean value for the saturated alkyl radicals, but the strength of the π-bond in olefins is about 59 kcal.[8] This means that the addition of $RO_2\cdot$ to an olefin will be exothermic by about 12 kcal.

$$RO_2 + >C=C< \underset{2b}{\overset{2a}{\rightleftarrows}} RO_2 >C—\dot{C}< + 12 \text{ kcal.} \quad \text{(III)}$$
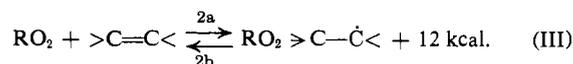
By the same methods used earlier, it can be shown that the entropy change for this type of process will be about -28 cal./mole °K., so that K_{eq} at 25° $\sim 10^3$ atm.$^{-1}$ ~ 1 mm.$^{-1}$ and K_{eq} (400°K.) ~ 1 atm.$^{-1}$. At $P_{O_2} \sim 0.1$ atm., these reactions will have ceiling temperatures of about 90°. If, on the other hand, the olefin is conjugated with other groups internally as in styrene or butadiene, then the $RO_2\cdot$ addition reaction will result in the formation of a resonance-stabilized benzyl or allyl radical, and the exothermicity increases by an additional 13 kcal.

$$RO_2 + >C=C—C=C< \underset{2b'}{\overset{2a'}{\rightleftarrows}} RO_2—C—\dot{C}—C=C< + 25 \text{ kcal.} \quad \text{(IV)}$$
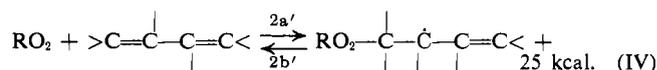
We see that the adducts of alkyl peroxy radicals to simple olefins will have low ceiling temperatures while adducts to conjugated or diolefins will have quite high ceiling temperatures. This is just the opposite behavior to that displayed by the addition of the alkyl radicals to O_2.

It is of some interest to look further into the kinetic behavior of the radicals formed in the addition reactions. Peroxy alkyl radicals with the free valence on the β-C atom (eq. III) are known to cyclize rather readily[16] so that the back reaction 2b in eq. III, must compete with the exothermic epoxidation reaction.

$$RO—O—C—C< \underset{4b}{\overset{4a}{\rightleftarrows}} RO\cdot + >\overset{O}{\overset{\diagup\diagdown}{C—C}}< + 13 \text{ kcal.} \quad \text{(V)}$$
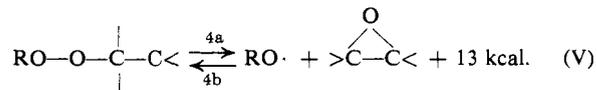
The Arrhenius parameters for reaction 2a can be estimated from similar addition reactions[13] to have an A factor of $10^{8.5}$ l./mole sec. and an activation energy of about 5 to 7 kcal. This would make the A factor for 2b about 10^{13} sec.$^{-1}$ and $E_{2b} \sim 18$ kcal. There is unfortunately no quantitative data on reactions such as (4a). The closest to it would be the thermoneutral reaction observed in the cyclization of 3-iodopropyl radical[17]

(16) M. Flowers, S. W. Benson, and L. Batt, *J. Chem. Phys.*, **37**, 2662 (1962).
(17) S. W. Benson, *ibid.*, **34**, 521 (1961).

$$ICH_2CH_2\dot{C}H_2 \longrightarrow I\cdot + \overset{\displaystyle CH_2}{\overset{\displaystyle \diagup \diagdown}{CH_2\text{---}CH_2}}$$
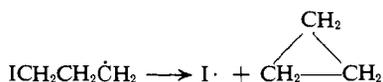
which has an activation energy of about 17 kcal. One would expect E for the exothermic reaction 4a to be less. A_{4a} can be expected to be about $10^{11.5}$ sec.$^{-1}$ so that if $E_{4a} \sim 14$ kcal. then reactions 4a and 2b will be reasonably competitive over a broad temperature range. Reaction 4a is the most reasonable explanation for epoxide formation in olefin oxidation. At higher temperatures (>350°) the epoxides will isomerize quite readily to aldehydes.[17,18]

In the case of the conjugated olefins, the simple epoxidation is no longer exothermic but is almost thermoneutral because of the loss of resonance energy.

$$R\text{---}O\text{---}O\text{---}\overset{|}{C}\text{---}\overset{|}{\dot{C}}\text{---}C{=}C{<} \xrightarrow{4a} R\dot{O} + \overset{\displaystyle O}{\overset{\displaystyle \diagup \diagdown}{\text{---}\overset{|}{C}\text{---}\overset{|}{C}\text{---}C{=}C{<}}} \quad (V')$$
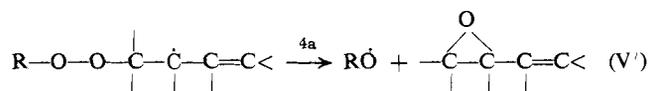
A kinetically more favorable path is

$$R\text{---}O\text{---}O\text{---}\overset{|}{\underset{|}{C}}\text{---}\overset{|}{\underset{|}{C}}\text{---}C{=}C{<} \xrightarrow{5} R\text{---}\dot{O} + \overset{\displaystyle O}{\overset{\displaystyle \diagup \diagdown}{{>}C\text{---}C{=}C\text{---}C{<}}}$$
$$+\ 20\ \text{kcal.} \quad (VI)$$
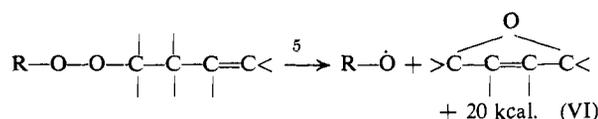
This reaction again should have an A factor of about $10^{11.5}$ sec.$^{-1}$ and an activation energy of about 10–15 kcal. These kinetic parameters would give the epoxidation reactions a reasonable kinetic speed somewhere between 100 and 200° when the concentration of O_2 is not too high. In gas phase reactions above 250° they would constitute an almost preferred path for diene oxidations.

H-Atom Abstraction Reactions of $RO_2\cdot$

The abstraction of H atoms by $RO_2\cdot$ is expected to be generally slow except from H atoms having weakly bound H atoms. Since $D°(RO_2\text{-H}) = 90 \pm 2$ kcal., we would expect rapid abstraction from tertiary C–H bonds with $D°({>}C\text{-H}) = 91.7$ kcal.[19]; from aldehydes with C–H bonds, 86 kcal.[20]; and from H–Br with a bond strength, 87 kcal. Abstractions from secondary C–H bonds (94.5 kcal.)[21] are expected to be fairly slow and of course much slower from primary C–H bonds (98 kcal.). Resonance weakened C–H bonds should provide easily abstractable H atoms and it has been well known that allylic and benzylic H atoms are easily chain oxidized to the corresponding hydroperoxides.[15] In both these latter cases the C–H bonds have strengths of about 84 kcal. A factors for all such reactions are expected to be like most H-atom abstractions, that is, about $10^{8\pm0.5}$ l./mole sec., although recent data[22] indicate that for some reason such A factors might tend towards the lower limit.

The activation energies for these might be expected to be about 6 kcal. for the exothermic H-atom abstractions and $\Delta H + 6$ for the endothermic. Thus $RO_2 + C_2H_6$ might be expected to have $E = 14$ kcal.

(18) S. W. Benson, *J. Chem. Phys.*, **40**, 105 (1964).
(19) H. Teranishi and S. W. Benson, *J. Am. Chem. Soc.*, **85**, 2887 (1963).
(20) H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, **36**, 2196 (1962); **37**, 540 (1963).
(21) P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2773 (1964).
(22) P. Gray and J. C. J. Thynne, "Tenth International Symposium on Combustion," Cambridge, England, 1964.

An equally interesting but generally neglected class of abstractions is the intramolecular. There has been very little specific attention devoted to this category although it is known that they are responsible for chain branching in low temperature radical polymerizations. From a structural point of view, saturated, six-membered rings have no strain, seven- and five-membered rings have about 7 kcal. of strain, while four- and three-membered rings have about 28 kcal. of strain.[17]

On this basis we may expect internal H-atom abstraction in $RO_2\cdot$ to occur from the γ-C atom with great facility, from the β-C atom much more slowly, and from the α-C atom possibly not at all. These reactions with their transition state are indicated below.
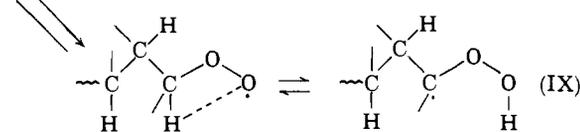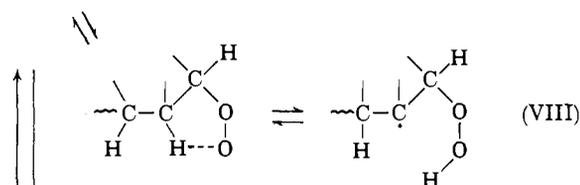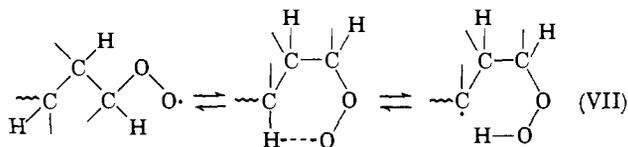
Now it is important to consider the thermochemistry in these systems since, if the rates of internal abstraction are significantly rapid compared to external reactions, then the reverse abstraction reactions will be even faster if the reactions are endothermic. The reason for this is that there is virtually no entropy change accompanying the over-all internal H-atom abstraction so that $K_{eq} = (\cdot RO_2H)/(RO_2\cdot) \approx 10^{-\Delta H/\theta}$ where $\theta = 2.303RT$ in kcal. If $\Delta H = 5$ kcal. and $\theta = 1.8$ kcal. (400°K.) as will be the case for H-atom abstraction from secondary $>CH_2$, then the $\cdot RO_2H$ form will be only 10^{-3} of the $RO_2\cdot$ form and the abstraction will be trivial. Thus we may expect that at low temperatures only abstraction from tertiary C–H bonds and resonance-weakened C–H bonds (allyl and benzyl) will be of significance.

An excellent example of this is provided by the work of Rust[23] on the liquid phase oxidation of doubly branched hydrocarbons at about 120°. From 2,4-dimethylpentane he obtained an 89% yield (based on O_2 consumed) of the corresponding 2,4-dihydroperoxide. From the 2,3-dimethylpentane, however, only a monoperoxide was obtained. There was very slight evidence for some attack on the unbranched 4-position, but this could well be a secondary product. From the other compounds he studied, he was able to show that internal attack at the α- and β-positions was negligible while there was some attack at the δ-C–H bond.

At much higher temperatures (350–500°) the proportion of hydroperoxide radical will increase, e.g., K_{eq}

(23) F. F. Rust, *J. Am. Chem. Soc.*, **79**, 4000 (1957).

$\sim 10^{-1.7}$ at 650°K. for the preceding case where $\Delta H = 5$ kcal. While the ($\cdot$ROOH) radical form is still small compared to the ($RO_2\cdot$) form it may now become an important species because at these higher temperatures, which usually involve vapor phase reactions, it may react much more rapidly than the $RO_2\cdot$. The bimolecular H-atom abstraction reaction of $RO_2\cdot$ from RH is slower in the gas phase, relative to solution reactions by factors of the order of 10^3 to 10^4, simply owing to the smaller concentrations of donor RH. In contrast the $\cdot RO_2H$ form can give cyclic ethers in a unimolecular reaction (eq. VII'). Similar

$$
\begin{array}{c}
\text{H} \qquad\qquad \text{H} \\
\text{C—C—H} \qquad\qquad \text{C—C—H} \\
\text{$\sim$C} \quad \text{O} \quad \xrightarrow{7} \quad \text{$\sim$C——O} + \dot{\text{O}}\text{H} \qquad\text{(VII')} \\
\text{O—H}
\end{array}
$$
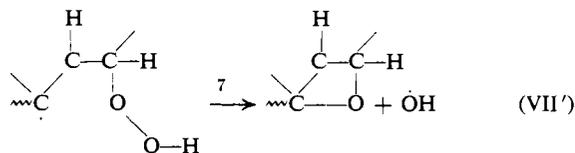
reactions can be written for the β- and δ- ($\cdot RO_2H$) radicals. Reaction 7 will be expected to have an A factor of about 10^{11} sec.$^{-1}$ and an activation energy of about 15 kcal. At 650°K. it will be about 200 times faster than the bimolecular H-atom abstraction by the $RO_2\cdot$ form and constitute a major reaction path.

These conclusions are supported by the work of Jones and Fenske[24] who showed that, at 365°, the vapor phase oxidation of C_6–C_{16} hydrocarbons gave about 11–25 wt. % of epoxides as products. From n-hexane, the C_6 epoxide fraction contained 59% tetrahydrofurans, 35% trimethylene oxides, and about 6% of 1,2-epoxides. From n-heptane they found among the C_7 epoxides, 68% of tetrahydrofurans, 26% trimethylene oxides, and again 6% of 1,2-epoxides.

The most interesting example of an internal abstraction which has been widely used in kinetic oxidation schemes corresponds to an over-all four-center reaction (eq. X). There is no direct evidence for such an over-all

$$
\begin{array}{c}
\text{H}\cdot\cdot\cdot\text{O} \ddagger \\
\text{R—C}\cdot\cdot\cdot\text{O} \\
\text{H} \\
\text{R—CH}_2\cdot + \text{O}_2 \longrightarrow \text{RCHO} + \text{OH} \qquad\text{(X)} \\
\text{H} \quad\text{H} \qquad\qquad \text{H} \\
(\text{R—C} \quad \text{O}\cdot)^* \rightleftharpoons (\text{R—C}\cdot \quad \text{H})^* \\
\text{O} \qquad\qquad \text{O—O}
\end{array}
$$
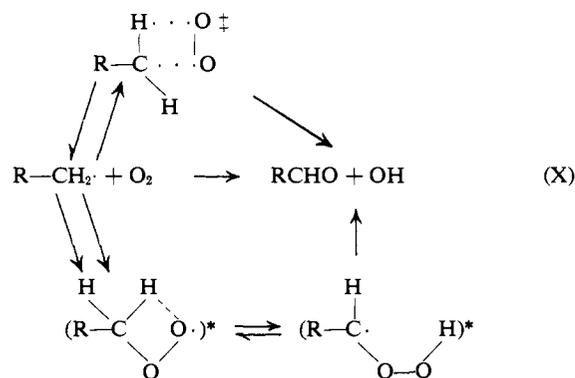
step which on structural grounds would be expected to have a fairly high activation energy and a fairly low A factor. The over-all reaction is exothermic by somewhere in the vicinity of 51 to 57 kcal./mole depending on R, but most of this energy is not released before the last step involving the formation of the carbonyl π-bond. If it were to occur in stages, the intermediate $RCH_2O_2\cdot$ radical would again not be expected to undergo α-C–H abstraction very readily. It has been argued that the initial $RCH_2O_2\cdot$ radical is vibrationally excited by about 28 kcal., and this would make the α-C–H abstraction very likely. Such a hot radical reaction is not necessarily probable, since energy loss

(24) J. H. Jones and M. R. Fenske, *Ind. Eng. Chem.*, **51**, 262 (1959).

via collision is a much more likely fate for the excess energy. In the cases where the reaction might have been observed, for CH_3 and C_2H_5,[12] no indication of its existence has been evident.[25]

Radical Reactions of $RO_2\cdot$ and Solvent Effects

Since $RO_2\cdot$ is a relatively inert radical it is expected to be an important participant in termination processes. Three different partner radicals are of generic interest, $RO_2\cdot$, $RO\cdot$, and $R\cdot$. At various times species such as R_2O_4 and R_2O_3 have been discussed as metastable intermediates[26] arising from termination, but the bulk of available evidence[10] indicates that R_2O_4 is extremely unlikely while R_2O_3 is plausible only at low temperatures. On the other hand, considerable evidence is available from both gas phase[2a,12] and solution[27a,b] studies to indicate that the dominant result of $2RO_2\cdot$ collision is $2RO\cdot + O_2$.

There is no reasonable structure of the R_2O_4 transition state which will lead to $R_2O_2 + O_2$ in one step, and on these grounds we have proposed that $2RO_2\cdot$ not be considered a terminating reaction.[27b] In solution, on the other hand, this reaction leads to the formation of $2RO\cdot$ radicals in the same solvent cage. Despite the fact that we have shown elsewhere[28] that the recombination of 2-t-BuO$\cdot$ to form the peroxide, (t-BuO$_2$–t-Bu) is about one-tenth as fast as a diffusion-controlled rate ($k_r = 10^{8.2}$ l./mole sec.), in the absence of any faster recombination processes, the small amount of cage effect (5–10%) accompanying $2RO_2\cdot \rightarrow 2RO\cdot + O_2$ could well account for termination.[29]

With $RO\cdot$, the only possible termination, again on structural grounds, would be disproportionation leading to RO_2H and either aldehyde or ketone. If, however, $RO\cdot$ is tertiary with no α-C–H bonds, then again no reasonable termination is possible.

(25) For contrary opinions, see, J. Farren, J. R. Gilbert, J. W. Linnett, and I. A. Read, *Trans. Faraday Soc.*, **60**, 740 (1964), and J. Heicklen and H. S. Johnston, *J. Am. Chem. Soc.*, **84**, 4030 (1962). We believe that in both these studies the evidence for reaction X is very indirect and possibly complicated by wall effects.

(26) S. W. Benson, *J. Chem. Phys.*, **33**, 306 (1960).

(27) (a) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2407 (1963); (b) C. A. McDowell and S. Sifniades, *Can. J. Chem.*, **41**, 300 (1963). These authors have demonstrated that in the gas phase photooxidation of CH_3CHO at 20° the reaction of 2 moles of CH_3CO_3 leads to the formation of O_2 and is essentially a termination reaction. They have assumed that the $(CH_3CO)_2$–O_2, which is observed as a termination product, is produced in the same act as the O_2 formation. However, an equally valid interpretation of their results is obtained if one assumes that the sequence is

$$2CH_3CO\text{–}O_2\cdot \xrightarrow{k_1} 2CH_3CO_2\cdot + O_2$$

$$2CH_3CO_2\cdot \xrightarrow{k_t} (CH_3CO)_2O_2$$
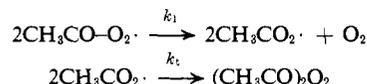
with the acetoxyl radicals undergoing predominantly termination rather than abstraction or decomposition. Both of these latter steps can be shown to be quantitatively compatible with the data of the above authors and other data [A. Rembaum and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 5975 (1954), and M. Levy and M. Szwarc, *ibid.*, **76**, 5981 (1954)] on the pyrolysis of acetyl peroxide. The photooxidation work was carried out under conditions favorable to termination, the chain lengths varying between one and two. The very large values of k_1 for acetoxyl radicals obtained by the authors are probably somewhat in error but they are not compatible with any four-center transition state as proposed by the authors. They are compatible with the above sequence in which k_t is the true termination step, but k_1 appears to be since the acetoxyl radical is a poor propagator at 20°.

(28) L. Batt and S. W. Benson, *J. Chem. Phys.*, **36**, 895 (1962); **38**, 3031 (1963).

(29) Dr. R. Hiatt (unpublished work) of this institute has indeed shown that these conditions are fulfilled in the chain decomposition of t-BuO$_2$H sensitized by di-t-butyl peroxalate. He finds the chain length virtually constant, independent of sensitizer or RO_2H concentration.

Reactions of $RO_2 \cdot$ + $R \cdot$ could lead to RO_2R excited by about 71 kcal. which is far in excess of the 37 kcal. needed to break the O–O bond. In solution this would not be important, and one would expect the excited RO_2R to thermalize far faster than the rate of bond rupture. In the gas phase, however, this is not the case, and we should expect a fair amount of rupture into $2RO \cdot$, depending on pressure, effectiveness of energy transfer, and the complexity of R.[30] For R more complex than C_2H_5 at temperatures below 100°, redissociation should be unimportant. On the other hand, disproportionation of $RO_2 \cdot$ + $R \cdot$ to give RO_2H + olefin may be expected to be important although

there are, unfortunately, no experimental data for comparison.

In the discussion thus far, except for the termination reactions, we have made no explicit distinctions between gas phase and solution reactions. In general, in nonpolar solvents, first-order Arrhenius parameters do not appear to differ greatly between gas phase and solution.[11] However, for "slow" second-order reactions, one expects A factors to be about an order of magnitude larger in solution than in the gas phase, reflecting essentially a free volume effect but is subject to so many uncertainities and corrections[31] that the expectation is not very strong for complex molecules. In fact, for these it is likely that the A factors should be about the same.

(30) Thus in the simplest case of $CH_3O_2CH_3$, using classical RRK theory of unimolecular reactions with 16 effective internal oscillators (see ref. 11, p. 231), we would expect about 50% redissociation of the excited species at 0.5 atm. pressure. For this calculation, we have used an A value of 10^{15} sec.$^{-1}$. For more complex R, the per cent will be lower.

(31) The chief uncertainty is that in forming $(A–B)\ddagger$ from $A + B$, one may replace free rotations of $(A–B)\ddagger$ by hindered rotations in solution and this could well outweigh the translation factors.

The Crystal Structure of Tetracyano-1,4-dithiin

W. A. Dollase

Contribution from the Crystallographic Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts. Received October 17, 1964

A crystal structure determination carried out on tetracyano-1,4-dithiin showed a folded molecule with approximate C_{2v} symmetry and a dihedral angle of 124°. All the atoms lie on one or the other of the dihedral planes. The interleaving of the molecules produces intermolecular distances as short as 3.1 Å.

A recently synthesized group of completely cyano-substituted, sulfur-containing heterocyclic compounds, containing only carbon, nitrogen, and sulfur, present several interesting structural problems. Their molecular configurations may be inferred by comparison with their parent heterocyclic compounds, but the exact details, such as the effect of the cyano group substitution, must be obtained from crystal structure analysis. A second, and generally more neglected, problem concerns the intermolecular structure of these compounds. A large number of structure determinations of molecular crystals containing hydrogen has shown that, in most cases, the formation of intermolecular hydrogen bonds strongly affects the intermolecular arrangement. The thiacyanocarbons, however, as members of the rather small number of hydrogen-free molecular compounds, provide a means of uncovering other factors which affect intermolecular structure but which are normally masked by the presence of hydrogen bonding.

With these problems in mind, the thiacyanocarbon tetracyano-1,4-dithiin (I) was chosen for a crystal structure analysis. The preparation and some of the properties of this compound are given by Simmons, *et al.*[1]

(1) H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R. Roland, and T. L. Cairns, *J. Am. Chem. Soc.*, 84, 4746 (1962).

I
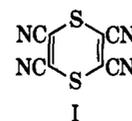
Experimental

The crystals are frequently elongated, yellow, transparent prisms.[2] Weissenberg photographs established the space group as $P2_1/n$, c unique. A least-squares refinement[3] of back-reflection Weissenberg film measurements gave the cell dimensions: $a = 6.953 \pm 0.002$, $b = 7.024 \pm 0.002$, $c = 18.498 \pm 0.005$ Å., $\gamma = 90.52 \pm 0.02°$.[4] The specific gravity was established by flotation as 1.59. This determined that there were four formula units/unit cell and suggested that the molecule was in the general position.

A crystal $0.020 \times 0.025 \times 0.025$ cm. was selected for intensity measurements; 850 integrated intensities were measured on a single crystal equi-inclination diffractometer employing Cu $K\alpha$ radiation and a geiger tube detector. The intensities were corrected for background, absorption, Lorenz, and polarization factors.

Examination of the Patterson function[5] gave the locations of two nonequivalent, relatively heavy sulfur atoms, verifying the general position of the molecule.

(2) A crystalline sample was kindly provided by Dr. H. E. Simmons.
(3) The calculations were performed with the aid of a computer program, LCLSQ, written by C. W. Burnham. (For this and other computer program references see "International Union of Crystallography, World List of Crystallographic Computer Programs," I.U.Cr. Commission on Crystallographic Computing, 1962.)
(4) It should be noted that the cell is very nearly *dimensionally* tetragonal which probably led to the incorrect preliminary X-ray results given by Simmons, *et al.*[1]
(5) All Fourier summations were made with ERFR2; W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende.