The Reversible Thermal Decomposition of Triphenylmethylperoxy Radical to Triphenylmethyl Radical and Oxygen[1]

Edward G. Janzen, F. J. Johnston, and Caroline L. Ayers[2]

Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30601. Received October 19, 1966

Abstract: The reaction of triphenylmethyl radical with oxygen in a solid lattice permeable to oxygen has been studied. The reaction is found to be reversible: $Ph_3C\cdot + O_2 \rightleftarrows Ph_3COO\cdot$. At room temperature under atmospheric oxygen pressure very little triphenylmethyl radical exists in equilibrium with the peroxy radical, but at 130° essentially no peroxy radical can be detected. Evacuation at room temperature converts the peroxy radical to triphenylmethyl radical. For the reaction of triphenylmethyl radical with oxygen $\Delta H = -9 \pm 1$ kcal/mole. An energy of activation for the thermal decomposition of triphenylmethylperoxy radical of 10.2 ± 1 kcal/mole is estimated.

In solution triphenylmethyl radical reacts with oxygen to yield triphenylmethyl peroxide.[3]

$$Ph_3C\cdot + O_2 \longrightarrow Ph_3COO\cdot \tag{1}$$

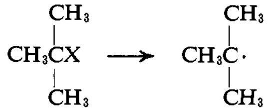
$$Ph_3COO\cdot + Ph_3C\cdot \longrightarrow Ph_3COOCPh_3 \tag{2}$$

Hydrogen atom donors may react with the intermediate peroxy radicals to form triphenylmethyl hydroperoxide.

$$Ph_3COO\cdot + RH \longrightarrow Ph_3COOH + R\cdot \tag{3}$$

We have found triphenylmethyl radical trapped in polycrystalline triphenylacetic acid and triphenylmethyl chloride or bromide reacts reversibly with oxygen to form the triphenylmethylperoxy radical. In the solid lattice the peroxy radical appears to be stable indefinitely at ambient temperatures in samples open to air. In a lattice permeable to oxygen it is possible to determine apparent equilibrium constants as a function of temperature and the heat of reaction for triphenylmethyl radical and oxygen. The activation energy for the decomposition of triphenylperoxy radical has also been estimated from a study of the rate of decomposition of the peroxy radical as a function of temperature.

In this study triphenylmethyl radicals were produced by γ radiolysis of triphenylmethyl chloride or bromide and triphenylacetic acid. Previous work has shown that γ radiolysis of alkyl halides[4] and tertiary carboxylic acids[5] produces alkyl radicals, *e.g.*



$$\mathrm{CH_3C(CH_3)_2X} \longrightarrow \mathrm{CH_3C(CH_3)_2\cdot} \tag{4}$$

where X = Cl, Br, I, COOH, or $COO^-NH_4^+$. Electron spin resonance spectra of a number of alkyl radicals have also been obtained from photolysis of certain alkyl iodides,[6-8] *e.g.*, methyl, ethyl, and propyl. Studies of alkyl radicals produced from alkyl halides were done at low temperatures in glassy or polycrystalline solids.[6,7] Carboxylic acids were irradiated at room temperature in single crystals or in polycrystalline samples.[5] In this work no reactions of the radicals with oxygen have been described. Either exposure to oxygen was avoided or diffusion of oxygen into the lattice is too slow to show significant reaction with the trapped radicals.

Radicals produced in certain polymers however have been found to react with oxygen and produce esr spectra attributed to peroxy radicals. Thus γ radiolysis of polytetrafluoroethylene produces a radical resulting from loss of fluorine atom. When irradiated in air or opened to air after irradiation under vacuum the spectrum contains peaks due to the peroxy radical.[9,10] The reaction of these radicals has been found

---

(1) Electron Spin Resonance Studies of Thermal Decomposition Mechanisms. Peroxides. II. Research sponsored by AFOSR (SRC)-OAR, U. S. A. F. Grant No. 1069-66, and in part by U. S. Public Health Service Research Grant RH-00206, Division of Radiological Health. For part I see C. L. Ayers, E. G. Janzen, and F. J. Johnston, *J. Am. Chem. Soc.*, **88**, 2610 (1966). For other thermal decomposition mechanism studies see E. G. Janzen, *ibid.*, **87**, 3531 (1965); E. G. Janzen and C. M. DuBose, Jr., *Tetrahedron Letters*, 2521 (1965).

(2) University of Georgia Alumni Foundation Fellow, 1965–1966.

(3) W. A. Waters, "Chemistry of Free Radicals," Oxford University Press, London, 1948, p 46; G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p 687; C. Walling, "Free Radicals in Solutions," John Wiley and Sons, Inc., New York, N. Y., 1957, p 408; E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 673; A. G. Davies, "Organic Peroxides," Butterworth & Co. Ltd., London, 1961, p 51; W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 290.

(4) T. Cole, H. O. Pritchard, N. R. Davidson, and H. M. McConnell, *Mol. Phys.*, 1, 406 (1958); B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958); P. B. Ayscough and C. Thomson, *Trans. Faraday Soc.*, **58**, 1477 (1962); P. B. Ayscough and H. E. Evans, *J. Phys. Chem.*, **68**, 3066 (1964); H. W. Fenrick, S. V. Filseth, A. L. Hanson, and J. E. Willard, *J. Am. Chem. Soc.*, **85**, 3731 (1963); H. W. Fenrick and J. E. Willard, *ibid.*, **88**, 412 (1966).

(5) H. Shields and P. Hamrick, *J. Chem. Phys.*, **42**, 443 (1965); Y. D. Tsvetkov, J. R. Rowlands, and D. H. Whiffen, *J. Chem. Soc.*, 810 (1964); J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

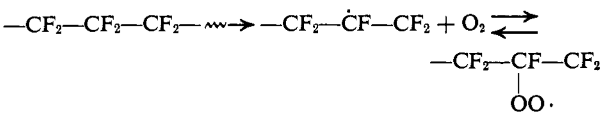
(6) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **34**, 1161 (1961); F. J. Adrian, E. L. Cochran, and V. A. Bowers, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 50.

(7) R. F. C. Claridge and J. E. Willard, *J. Am. Chem. Soc.*, **87**, 4992 (1965); R. H. Luebbe, Jr., and J. E. Willard, *ibid.*, **81**, 761 (1959).

(8) J. Turkevich and Y. Fujita, *Science*, **152**, 1619 (1966); M. Fujimoto, H. D. Gesser, B. Garbutt, and A. Cohen, *ibid.*, **154**, 381 (1966).

(9) (a) W. B. Ard, H. Shields, and W. Gordy, *J. Chem. Phys.*, **23**, 1727 (1955); H. N. Rexroad and W. Gordy, *ibid.*, **30**, 399 (1959); (b) R. J. Abraham and D. H. Whiffen, *Trans. Faraday Soc.*, **54**, 1291 (1958); (c) T. Matsugashita and K. Shinohara, *J. Chem. Phys.*, **32**, 954 (1960); **35**, 1652 (1961); (d) Z. Kuri, H. Ueda, and S. Shida, *ibid.*, **32**, 371 (1960); Z. Kuri and H. Ueda, *J. Polymer Sci.*, **50**, 349 (1961); H. Ueda, Z. Kuri, and S. Shida, *ibid.*, **A1**, 3537 (1963); (e) D. W. Ovenall, *J. Chem. Phys.*, **38**, 2448 (1963); *J. Phys. Chem. Solids*, **26**, 81 (1965); (f) Y. D. Tsvetkov, Y. S. Lebedev, and V. V. Voevodskii, *Vysokomolekul. Soedin.*, **1**, 1519, 1634 (1959); **3**, 882 (1961); *Chem. Abstr.*, **54**, 10468, 19123 (1960); **55**, 27947 (1961); (g) P. Barnaba, D. Cordischi, A. D. Site, and A. Mele, *J. Chem. Phys.*, **44**, 3672 (1966) (polytetrafluoroethylene oxide in this case); (h) R. Lontz, *Bull. Am. Phys. Soc.*, **8**, 328 (1963) ($CF_3CF_2\cdot CONH_2$ in this case).

(10) Oxy radicals are also thought to be present[9c,g] but this interpretation has been questioned by Ovenall.[9e]



$$\text{—CF}_2\text{—CF}_2\text{—CF}_2\text{—} \rightsquigarrow \text{—CF}_2\text{—}\dot{\text{C}}\text{F—CF}_2 + \text{O}_2 \rightleftarrows \text{—CF}_2\text{—}\underset{\text{OO}\cdot}{\underset{|}{\text{CF}}}\text{—CF}_2 \quad (5)$$

to be reversible.[9b-d,f] Under vacuum the peroxy radical decomposes partially at 150° and completely at 250° to produce the initial radical. The peroxy radical reappears upon cooling in air. Quantitative information has been difficult to obtain possibly because of the complexity of the perfluoroalkyl radical spectrum or because of some instability of the radical system at the temperatures required for alkylperoxy radical decomposition. However rates of the forward and reverse reaction have been calculated and the heat of reaction (eq 5) determined[9f] ($\Delta H = -14$ kcal).

Polycrystalline samples of tris(*p*-nitrophenyl)methyl radical react slowly with oxygen to give spectra of the peroxy radical.[11] Both radicals decay slowly but disappear completely after 48 hr. Evacuation of the sample removes the peroxy radical. These results were interpreted in terms of the following reactions.

$$(\text{NO}_2\text{C}_6\text{H}_4)_3\text{C}\cdot + \text{O}_2 \longrightarrow (\text{NO}_2\text{C}_6\text{H}_4)_3\text{COO}\cdot \quad (6)$$

$$(\text{NO}_2\text{C}_6\text{H}_4)_3\text{COO}\cdot + (\text{NO}_2\text{C}_6\text{H}_4)_3\text{C}\cdot \longrightarrow (\text{NO}_2\text{C}_6\text{H}_4)_3\text{COOC}(\text{C}_6\text{H}_4\text{NO}_2)_3 \quad (7)$$

An alternate explanation is that reaction 6 is reversible and evacuation displaces the equilibrium from right to left. The surprising observation that tris(*p*-nitrophenyl)methylperoxy radical can be seen in a host which itself is a radical may be evidence that reaction 7 is also reversible.

Electron spin resonance spectra of peroxy radicals have also been obtained by ultraviolet irradiation of a single crystal of α-tetralin hydroperoxide,[12] *t*-butyl and ethyl hydroperoxide glasses,[12] liquid *n*-butyl, *sec*-butyl, *t*-butyl, and cumene hydroperoxides,[12] and *t*-butyl, cumene, and methyldiphenylmethyl hydroperoxides in solution.[13] The reaction of radicals with oxygen in solution also provides enough peroxy radicals to be detected by esr, *e.g.*, cumyl peroxy,[14] alkyl peroxy,[15] and hydroxyalkyl peroxy.[16]

The *g* values of peroxy radicals are found to be considerably higher than *g* values for alkyl radicals (2.01 as compared to 2.003). For alkylperoxy radicals *g* values fall in the range 2.0137–2.0155.[12] The high *g* values for peroxy radicals make esr studies particularly convenient when detection of both alkyl and peroxy radicals is desired since peroxy radicals appear at much lower fields than most free radicals commonly encountered.[17] The line width of peroxy radicals varies between 2 and 36 gauss depending on temperature, viscosity, and structure of the alkyl group.[13] The line width is thought to depend on spin–orbit relaxation effects.[13]

Experimental Section

Powdered samples of triphenylmethyl derivatives were irradiated in a sample tube constructed as described by Adler.[18] An esr tube (Varian Associates) was connected to a 10-mm Pyrex tube by means of a graded seal. Approximately 0.05 g of the sample was introduced into the Pyrex end of the cell without allowing any of the compound to enter the esr tube. The cell was evacuated, sealed, and irradiated. Before measurements were made the esr tube was annealed with a hand torch because strong signals, presumably due to color centers in the quartz, developed in the walls of the esr tube. If no carbonaceous material has entered the esr tube the signals can be removed readily by heating.

High-energy radiation was provided by a Gammacell 200 cobalt-60 γ source. The radiation time varied from 15 to 60 min. The dose rate, measured by ferrous sulfate dosimetry, was 4.5×10^{17} ev g^{-1} min^{-1}. A Hanovia SC-2537 mercury vapor lamp was used for photolysis experiments. An ordinary vacuum, leak-tester Tesla coil was used to subject the surface of samples to electric discharge. Esr spectra were obtained using a Varian 4502 epr spectrometer with 12-in. magnet. The *g* values reported were measured by means of a dual cavity using diphenylpicrylhydrazyl as a *g*-value marker (*g* value $= 2.0036 \pm 0.002$).[19] These *g* values were checked utilizing a Magnion G502 nmr precision gaussmeter, a Hewlett-Packard 5245L frequency counter with 5253B frequency converter, and a Hewlett-Packard 540B transfer oscillator when this equipment became available.

Samples were heated in the spectrometer cavity by preheated nitrogen in a quartz dewar. The temperature was controlled by a V-4540 variable-temperature controller purchased as a spectrometer accessory from Varian Associates. Temperature was monitored during an experiment with an iron–constantan thermocouple inserted as near to the sample as possible without disrupting the balance of the cavity. These readings were checked by placing the thermocouple into an empty esr cell under the same conditions with the spectrometer off.

The difficulty in obtaining quantitative information using esr techniques is well recognized. In the determination of the heat of reaction for triphenylmethyl and oxygen "apparent" equilibrium constants were calculated in terms of arbitrary recorder chart paper units. The vertical distance from maximum to minimum was taken as proportional to the numbers of spins in the cavity. In order to test the validity of this assumption a plot of peak height as a function of free radicals trapped in a polycrystalline solid was made using sodium dithionite[20] as the radical-containing solid. The plot was linear in the range 0.010–0.055 g. In addition a plot of the peak height of triphenylmethyl radicals in triphenylacetic acid as a function of radiation dose was found to be linear over a radiation time range of 30 min. The number of radicals formed during γ radiation is expected to be proportional to the time of radiation at least for relatively short radiation periods. These results are thought to adequately show that the observed peak height can be correlated with the number of radicals present in the sample. The data obtained for the plots include the additional potential error resulting from small changes in spectrometer performance when samples are changed. This source of error was eliminated by obtaining all the information from one sample which was not removed from the cavity during heating at different temperatures.

Since at most temperatures investigated the spectrum of both triphenylmethyl and triphenylmethylperoxy radical were obtained, it would appear that the peak heights of both radicals could be measured as a function of temperature and used in the determination of the equilibrium constant. It was not possible to do this explicitly, however, because of the different saturation properties of the two radicals. Under normal operating conditions using the usual Varian high-power microwave bridge (10 db attenuation) the triphenylmethyl radical signal is partly saturated, *i.e.*, the peak height decreases with increase in microwave power. The peroxy peak does not appear to saturate under any power conditions, *i.e.*, the peroxy peak height increases with increase in microwave power. Because of these very different saturation properties it might be expected that changes in temperature and "concentration" (number of spins per unit volume of solid) might affect

---

(11) F. M. Schimmel and F. W. Heineken, *Physica*, **23**, 781 (1957).

(12) K. U. Ingold and J. R. Morton, *J. Am. Chem. Soc.*, **86**, 3400 (1964). See also L. H. Piette and W. C. Landgraf, *J. Chem. Phys.*, **32**, 1107 (1960).

(13) J. R. Thomas, *J. Am. Chem. Soc.*, **88**, 2064 (1966).

(14) Y. S. Lebedev, V. F. Tsepalov, and V. Y. Shlyapintokh, *Proc. Acad. Sci., USSR, Phys. Chem. Sect.*, **139**, 646 (1961) (Consultants Bureau English Translation); J. R. Thomas, *J. Am. Chem. Soc.*, **85**, 591 (1963); M. Bersohn and J. R. Thomas, *ibid.*, **86**, 959 (1964).

(15) R. W. Fessenden and R. N. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(16) R. Livingston and H. Zeldes, *ibid.*, **44**, 1245 (1966).

(17) This point has been emphasized by Bersohn and Thomas;[14] see, however, Ingold and Morton.[12]

(18) G. Adler, D. Ballantine, and B. Baysal, *J. Polymer Sci.*, **48**, 195 (1960).

(19) A. N. Holden, W. A. Yager, and F. R. Merritt, *J. Chem. Phys.*, **19**, 1319 (1951).

(20) Commerical sodium dithionite contains approximately 0.1% $\text{SO}_2\cdot^-$ trapped in the crystal lattice; unpublished work in our laboratories.

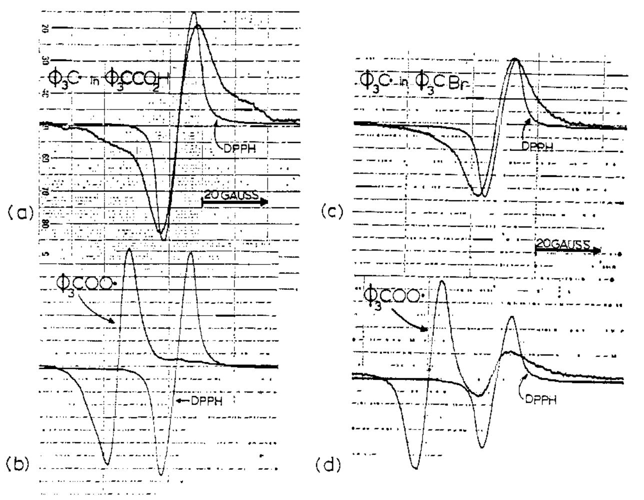


Figure 1. Electron spin resonance signals of triphenylmethyl radicals produced by γ radiolysis of (a) triphenylacetic acid (15 min) and (c) triphenylmethyl bromide (30 min); (b) γ radiolysis of triphenylacetic acid open to air; (d) formation of triphenylmethylperoxy radical from triphenylmethyl radical shown in (c) after 135-min exposure to air. DPPH is used as g-value marker.

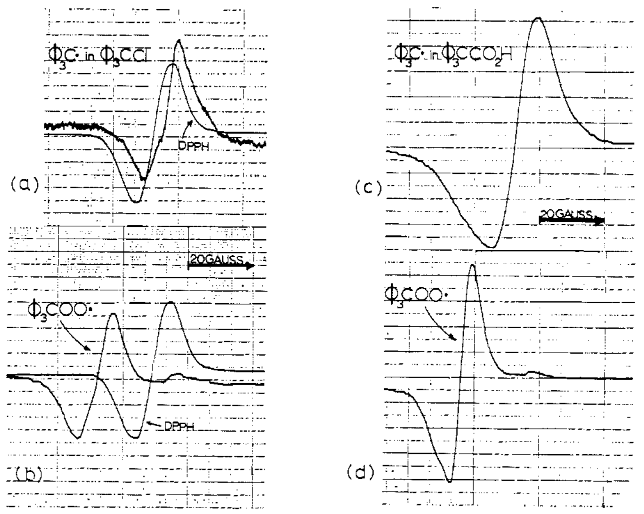


Figure 2. Electron spin resonance signals of triphenylmethyl and triphenylmethylperoxy radicals: (a) ultraviolet irradiation of triphenylmethyl chloride for 88.5 hr; (b) formation of triphenylmethylperoxy radical from triphenylmethyl radical shown in (a) after 90-min exposure to air; (c) triphenylacetic acid subjected to Tesla coil discharge for 1.5 min; (d) triphenylmethylperoxy radical formed immediately upon exposing triphenylmethyl radicals shown in (c) to air.

the peak height of the two radicals differently. For these reasons only the peak height of the peroxy radical was used in this work. The total number of triphenylmethyl radicals was taken as equal to the number of peroxy radicals in a sample when no signal from triphenylmethyl radical could be detected (*e.g.* room temperature open to atmospheric oxygen). The signal due to the triphenylmethyl radicals at any temperature is $(\mathrm{Ph_3COO}\cdot)_0 - \mathrm{Ph_3COO}\cdot$, where $(\mathrm{Ph_3COO}\cdot)_0$ is the peak height due to peroxy radical when no triphenylmethyl radical is present (or at least 100-fold less than triphenylmethylperoxy) and $\mathrm{Ph_3COO}\cdot$ is the peak height measured for peroxy radical at any temperature.

At normal microwave powers the peroxy radical peak height is greater than the triphenylmethyl peak height for a given number of radicals. This observation could be mistakenly attributed to a chemical reaction which generates more peroxy radicals than triphenylmethyl radicals initially present in the sample. However the observed peak heights (actually the areas under the integrated curves) are also proportional to relaxation times for the respective spin states of each radical and should be measured at a microwave power where no saturation occurs. Our measurements of peaks for peroxy radical only obviates the need to do this, but caution should be used in comparing relative concentrations of different types of radicals from peak heights obtained at the same level of microwave power.

Triphenylmethyl chloride (Matheson Coleman and Bell), triphenylmethyl bromide (Columbia Organic Chemicals Co., Inc.), and triphenylacetic acid (Aldrich Chemical Co., Inc.) were used without further purification.

Results

The γ radiolysis of powder samples of triphenylacetic acid and triphenylmethyl chloride and bromide under vacuum produces a strong esr signal with g value = 2.0024. Figures 1a and c show the signals obtained from triphenylacetic acid and triphenylmethyl bromide. The line width is 10.7 gauss (measured from maximum to minimum). Irradiation in air gives a strong symmetric signal with g value = 2.0146 (*e.g.*, Figure 1b in triphenylacetic acid). The line width is 7.4 gauss. When a sample irradiated under vacuum is opened to air the signal at g = 2.0024 diminishes in intensity with simultaneous appearance of the signal at g = 2.014 (*e.g.*, Figure 1d in triphenylmethyl bromide).

The signal obtained upon radiolysis of these triphenylmethyl derivatives is undoubtedly due to triphenylmethyl radical. Its formation is consistent with previous studies in radiolysis of tertiary alkyl halides and carboxylic acids.[4,5] The observed g value and saturation properties (see Experimental Section) also are characteristic of hydrocarbon free radicals. The reaction of triphenylmethyl radical with oxygen in air gives the triphenylmethylperoxy radical. The g value[12] and line width[21] are in excellent agreement with published values for other peroxy radicals.

Triphenylmethyl radical is also produced by irradiation with ultraviolet light or subjecting any of the solids to electric discharge of a Tesla coil (*e.g.*, Figures 2a and c). The signals are more asymmetric for both triphenylmethyl and triphenylmethylperoxy radicals.

Triphenylmethyl radical reacts with oxygen to yield the peroxy radical at different rates depending on the parent compound used and on the means of radical production. The relative rates of peroxy radical formation in the hosts triphenylacetic acid and triphenylmethyl chloride and bromide are shown in Figure 3. At ambient temperatures and at atmospheric oxygen pressure the conversion to the peroxy radical is at least 95% within 30 min in triphenylacetic acid. At the spectrometer settings used for the peroxy radical in triphenylacetic acid essentially no triphenylmethyl signal is recorded (Figures 1b and 2d). The rate of peroxy radical production in triphenylmethyl chloride or bromide is much slower. γ Radiolysis of sodium triphenylacetate gives a weak signal due to the triphenylmethyl radical but the appearance of the peroxy radical is very slow. Triphenylmethyl radical produced from photolysis of silver triphenylacetate does not produce any detectable peroxy radical.[22] It appears that the rate of diffusion of oxygen into the lattice of triphenylmethyl derivatives decreases in the order

$$\mathrm{Ph_3CCOOH} \gg \mathrm{Ph_3CBr} > \mathrm{Ph_3CCl} > \mathrm{Ph_3CCOO^-Na^+} \gg \mathrm{Ph_3CCOO^-Ag^+}$$

---

[21] If measured from inflection point to inflection point the peroxy line width is 15 gauss, which is in good agreement with the line width for *t*-butylperoxy radical in a highly viscous solvent.[13]

[22] Preliminary results of Dr. Richard Kriens.

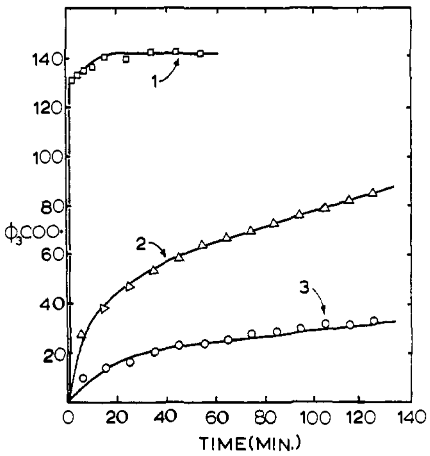


Figure 3. Triphenylmethylperoxy radical formation (in arbitrary recorder chart paper units) as a function of time in triphenylacetic acid (1), triphenylmethyl bromide (2), and triphenylmethyl chloride (3) at room temperature. Triphenylmethyl radicals were produced by γ radiolysis of samples under vacuum. The triphenylmethylperoxy signal was recorded immediately after opening the samples to air.

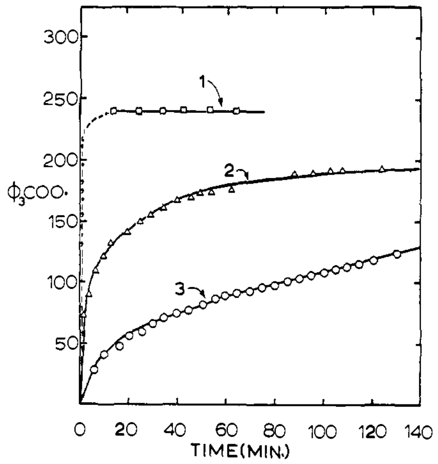


Figure 4. Triphenylmethylperoxy radical formation (in arbitrary recorder chart paper units) as a function of time in triphenylmethyl chloride at room temperature. Triphenylmethyl radicals were produced by Tesla coil discharge (1), photolysis (2), and γ radiolysis (3) of samples under vacuum. The triphenylmethylperoxy signal was recorded immediately after opening the samples to air.

Triphenylacetic acid would seem to have the most "open" lattice at least toward diffusion of oxygen. Unfortunately information regarding the crystal structure of these compounds is unavailable.

The observed rate of formation of triphenylmethylperoxy radical in a given sample also depends on the method of producing triphenylmethyl radicals. Thus the appearance of peroxy radicals is most rapid in samples subjected to a Tesla coil discharge, somewhat slower for photolyzed samples, and slowest for samples exposed to γ radiation. The relative rates of peroxy radical production in triphenylmethyl chloride are shown in Figure 4. Radicals generated from a Tesla coil discharge are known to be located only on the surface of particles.[23] The observed rates of peroxy radical formation are in agreement with this picture. Radicals formed on the surface of the particle are most accessible and react rapidly with oxygen, whereas radicals formed randomly in the interior of the solid from γ radiolysis are least accessible and react more slowly because of the limiting rate of diffusion of oxygen into the solid lattice. Photolysis probably forms radicals on the surface and in the interior, and the observed rate is intermediate.

The conversion of triphenylmethyl radicals to peroxy radicals is essentially complete at ambient temperatures. However at higher temperatures triphenylmethylperoxy radical decomposes to yield triphenylmethyl radical. The peak height due to the peroxy radical diminishes in intensity with increase in temperature while the triphenylmethyl radical increases. Both radicals are readily detected at temperatures up to 130°. At this temperature essentially complete conversion to triphenylmethyl radical has occurred. If left open to air the peroxy radical reappears upon cooling. The same peak height is obtained upon cooling as observed during previous heating. At least three sequences of heating and cooling do not significantly diminish the total number of radicals in a given sample of triphenylacetic acid. A considerable loss of radicals is observed, however, when triphenylmethyl chloride or bromide is used as a host.

These results clearly show that triphenylmethylperoxy radical is in equilibrium with triphenylmethyl radical and oxygen at commonly used temperatures.

$$\mathrm{Ph_3COO\cdot} \rightleftharpoons \mathrm{Ph_3C\cdot} + \mathrm{O_2} \qquad (8)$$

The existence of this equilibrium is further supported by the observation that the triphenylmethylperoxy radical disappears upon evacuation of the sample and reappears when air or oxygen is readmitted. The rate of disappearance of triphenylperoxy radical as a function of temperature under vacuum is discussed in a following paragraph.

In triphenylacetic acid the triphenylmethyl–triphenylmethylperoxy system is stable enough and equilibrium is attained rapidly enough over a convenient temperature range to allow a detailed study of the equilibrium constant as a function of temperature to be made. Thus the peak heights of the peroxy radical at equilibrium with atmospheric oxygen were measured as a function of temperature. Initial treatment involved measurements of both the triphenylmethyl and peroxy peak height as a function of temperature, but this proved to be unsatisfactory probably because of the large difference in saturation properties of the hydrocarbon radical and the peroxy radical (see Experimental Section). Only the peroxy peak heights were subsequently used. The peak height of peroxy radical in the absence of triphenylmethyl radical is taken as a measure of the available triphenylmethyl radicals: $(\mathrm{PhCOO\cdot})_0$. An apparent equilibrium constant can be calculated using arbitrary recorder chart paper units and assuming the pressure of oxygen constant.

$$K(\text{apparent}) = \frac{(\mathrm{Ph_3COO\cdot})_0 - \mathrm{Ph_3COO\cdot}}{\mathrm{Ph_3COO\cdot}} \qquad (9)$$

A plot of the logarithm of K(apparent) as a function of the inverse absolute temperature yields ΔH for the decomposition of the peroxy radical (eq 8). Figure 5 shows such a plot of peroxy radical in triphenylacetic acid using γ radiolysis to generate triphenylmethyl

---

(23) C. H. Bamford, A. D. Jenkins, and J. C. Ward, *Nature*, **186**, 712 (1960); *J. Polymer Sci.*, **48**, 37 (1960).

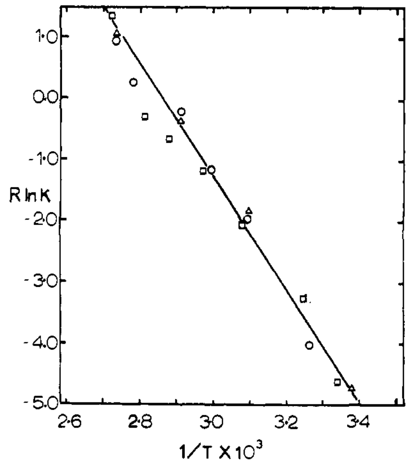


Figure 5. Plot of $R \ln K$(apparent) *vs.* $1/T$ for $Ph_3COO\cdot \rightleftharpoons Ph_3C\cdot + O_2$ in triphenylacetic acid open to air. The symbols O, □, and Δ designate different heating sequences of the same sample.

radicals. More scatter of points is evident at the higher temperatures because of the difficulty in accurately measuring the small peak height for the remaining peroxy radical. The slope of the line as obtained from a least-squares fit gives $\Delta H = 9.0$ kcal/mole. Similar measurements were made on a sample of triphenylacetic acid subjected to a Tesla coil discharge. Here the radicals are located on the surface of the particles; $\Delta H = 8.3$ kcal/mole in this case. The difference is probably within the error of the ΔH determination.

The effect of oxygen pressure on the equilibrium reaction 8 was also investigated. The peroxy peak height varied with oxygen pressure as shown in Figure 6. An apparent saturation concentration of peroxy radical is reached at 20, 50, and 100 mm at 28, 62, and 91°, respectively. The behavior at any one temperature is consistent with a Langmuir pattern of adsorption of oxygen at lattice sites throughout the crystal. Because of the evident permeability of the solid to oxygen, this picture is not unreasonable.[24] The curves in Figure 6 were obtained with the same sample but at different times and may not be strictly compared. They do, however, show a decrease in the saturation concentration of peroxy radical with an increase in temperature and suggest that the equilibrium reaction involves radicals and "adsorbed" oxygen molecules. The suggested processes may be summarized as follows

$$O_{2(g)} + S \rightleftharpoons O_{2(ads)} \qquad (10)$$

$$(O_2)_{ads} = kP_{O_2}/(1 + kP_{O_2}) \qquad (11)$$

$$O_{2(ads)} + Ph_3C\cdot \rightleftharpoons Ph_3COO\cdot \qquad (12)$$

$$K = Ph_3COO\cdot/(O_2)_{ads}Ph_3C\cdot \qquad (13)$$

where oxygen adsorbed at a lattice site (S) is $O_{2(ads)}$. If the total concentration of radicals, [M], = $Ph_3COO\cdot + Ph_3C\cdot$ and if $(O_2)_{ads} >> [M]$ then

$$\frac{K(kP_{O_2})}{1 + kP_{O_2}} = \frac{(Ph_3COO\cdot)}{[M] - (Ph_3COO\cdot)} \qquad (14)$$

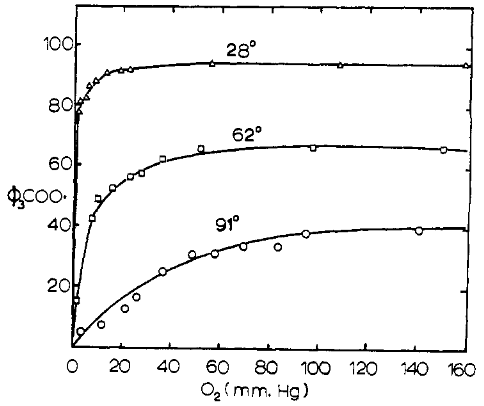


Figure 6. Triphenylmethylperoxy radical formation (in arbitrary recorder chart paper units) as a function of oxygen pressure at different temperatures. Triphenylmethyl radicals were produced by γ radiolysis of triphenylacetic acid under vacuum.

The form of this equation is consistent with the observed dependence of $Ph_3COO\cdot$ on oxygen pressure. For example, the data at 62 and 91° may be represented, within experimented error, by $Ph_3COO\cdot = 9.45P_{O_2}/[1 + 0.13P_{O_2}]$ and $Ph_3COO\cdot = 1.72P_{O_2}/[1 + 0.043\cdot P_{O_2}]$, respectively. At sufficiently high oxygen pressures

$$K = Ph_3COO\cdot/([M] - Ph_3COO\cdot) \qquad (15)$$

K is K(apparent)$^{-1}$ if [M] is $(Ph_3COO\cdot)_0$ in eq 9. The temperature dependence of K corresponds to a ΔH of -9.0 kcal/mole for reaction 11.

Attempts were made to study the kinetics of reaction 8. In these experiments samples containing only peroxy radicals were heated under evacuation as rapidly as possible to the desired temperature and the rate of conversion to triphenylmethyl radical followed. Under the conditions of the experiment a residual pressure of 1–3 mm of O_2 was present in the system and in each experiment the system approached an equilibrium situation dependent upon the temperature and residual oxygen pressure. Although quantitative kinetic data were not obtained, the following treatment gave what is felt to be meaningful results.

The peak heights due to peroxy radical as a function of time are shown in Figure 7 for experiments at several temperatures. Reaction 8 was considered as first order in the forward direction (k_1) and pseudo first order in the reverse direction (k_2) with $(O_2) >> Ph_3COO\cdot + Ph_3C\cdot$. Standard kinetic treatment gives

$$(k_1 + k_2) = -1/t \ln\{(R\cdot)_e(RO_2\cdot) - (RO_2\cdot)_e(R\cdot)/(R\cdot)_e[M]\} \qquad (16)$$

where $(R\cdot)_e$ and $(RO_2\cdot)_e$ represent equilibrium concentrations of $Ph_3C\cdot$ and $Ph_3COO\cdot$, respectively. [M] is the constant total radical concentration. Plots of $\ln[(R\cdot)_e(RO_2\cdot) - (RO_2\cdot)_e(R\cdot)]$ *vs.* t are shown in Figure 8. From the apparent equilibrium constant for each experiment, $K = k_1/k_2$, values of k_1 were obtained at each temperature. Figure 9 shows a plot of $R \ln k_1$ *vs.* $1/T$. The slope corresponds to an apparent activation energy of 10.2 ± 1 kcal/mole. This value is consistent with the observed ΔH for the reaction if one assumes essentially zero activation energy for the recombination process. Although rather gross as-

(24) A similar adsorption picture has been presented in the study of the reaction of nitric oxide with radicals produced in γ-irradiated polytetrafluoroethylene.[9d] However, for the reaction of radicals in γ-irradiated polyethylene with hydrogen, radical decay was found to be linear as a function of hydrogen pressure (M. G. Omerwood, *Polymer*, 4, 451 (1963).

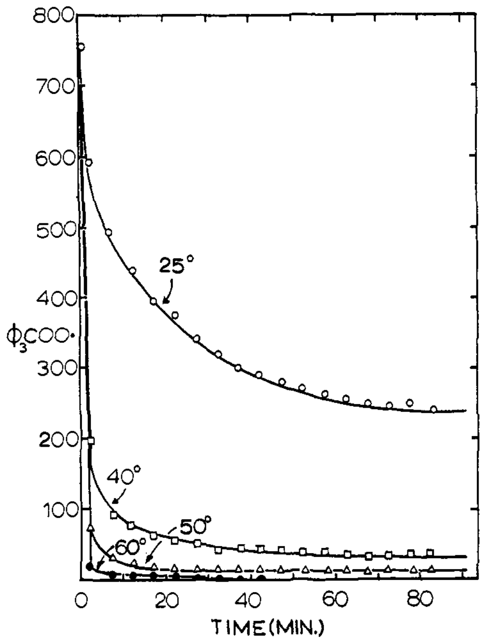


Figure 7. Triphenylmethylperoxy radical decomposition (in arbitrary recorder chart paper units) as a function of time in triphenylacetic acid at different temperatures during continuous evacuation. Samples of triphenylmethylperoxy radicals were obtained by allowing samples containing triphenylmethyl radicals (produced by γ radiolysis) to react with air.

sumptions are made in this treatment, the over-all behavior and consistency of the results suggest that they are not completely unreasonable.

Discussion

The possible reversibility of the reaction of oxygen with free radicals has not generally been considered.[3]

$$R\cdot + O_2 \rightleftarrows ROO\cdot \qquad (17)$$

The rate of the reaction of radicals with oxygen is normally very fast and leads to peroxy radicals which in solution or in the gas phase undergo further reactions themselves.

$$ROO\cdot \xrightarrow{R\cdot} ROOR \qquad (18)$$

$$ROO\cdot \xrightarrow{RH} ROOH \qquad (19)$$

$$ROO\cdot \xrightarrow{ROO\cdot} 2RO\cdot + O_2 \qquad (20)$$

These subsequent reactions are usually fast and irreversible. For stabilized radicals the reaction with oxygen might be expected to be reversible. Hendry and Russell[25] have come to this conclusion in studies of retardation of cyclohexene autoxidation by polyarylmethanes, *e.g.*, using triphenylmethane. Inhibition was attributed to termination steps involving triphenylmethyl and cyclohexenylperoxy radicals.

$$C_6H_9OO\cdot + Ph_3CH \longrightarrow C_6H_9OOH + Ph_3C\cdot \qquad (21)$$

$$Ph_3C\cdot + O_2 \rightleftarrows Ph_3COO\cdot \qquad (22)$$

$$Ph_3C\cdot + C_6H_9OO\cdot \longrightarrow Ph_3COOC_6H_9 \qquad (23)$$

The rapid reversibility of reaction 8 would provide a constant source of triphenylmethyl radicals for termination reactions. The observation that at 90° inhibition was more pronounced than at 60° supports this explanation since at higher temperatures more triphenylmethyl radicals would be expected to persist in solution in equilibrium with the peroxy radicals. In this study attempts were made to quench the equilibrium reaction 8 with hydrogen bromide, but these attempts were probably unsuccessful[26] since inhibition of the autoxidation continued in the presence of a hydrogen bromide source.

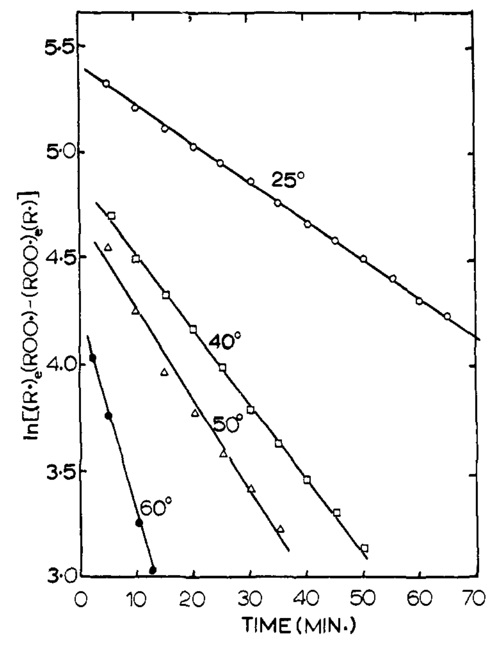


Figure 8. Plot of ln [(R·)$_e$(ROO·) − (ROO·)$_e$(R·)] as a function of time for decomposition of triphenylmethylperoxy radical (data and conditions as in Figure 7).

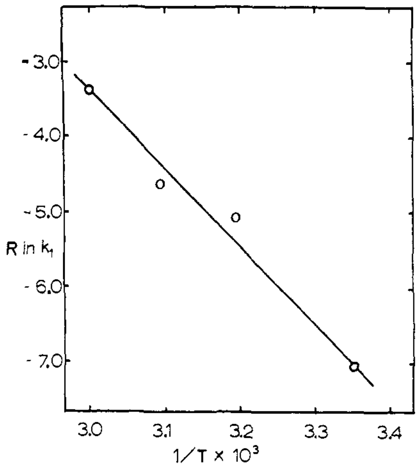


Figure 9. Plot of R ln k_1 *vs.* $1/T$ for decomposition of triphenylmethylperoxy radical to triphenylmethyl radical and oxygen (data and conditions as in Figures 7 and 8).

Russell has further pointed out[25] that the reversibility of reaction 17 provides a good explanation for the observed dimerization and disproportionation of numerous reactive radicals at elevated temperatures in the presence of oxygen, *e.g.*, benzyl, methyl, etc.

Our results provide the first experimental evidence for the reversibility of reaction 22 for triphenylmethyl

---

[25] D. G. Hendry and G. A. Russell, *J. Am. Chem. Soc.*, **86**, 2371 (1964); G. A. Russell in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers Inc., New York, N. Y., 1962, p 110.

[26] Private communication from Professor G. A. Russell.

radical and oxygen. In a solid lattice permeable to oxygen we estimate approximately one-third of the total number of radicals are triphenylmethyl radicals in equilibrium with peroxy radicals at 60° and atmospheric oxygen pressure. At 90° approximately two-thirds are triphenylmethyl radicals. If these results can be applied to radicals in solution at 90° it would appear that the concentration of triphenylmethyl radicals would exceed the concentration of peroxy radicals by approximately two times at equilibrium. These observations point out the need to consider many reactions of aralkyl radicals with oxygen as reversible at commonly used temperatures.

The reaction of triphenylmethyl radical and oxygen in a solid lattice (*viz.* triphenylacetic acid) is exothermic by 9 kcal/mole. Whether this value is applicable to the chemistry of triphenylmethyl radical in the gas phase (or in solution in the absence of solvent effects) will depend on (1) the similarity of the heats of sublimation for the triphenylmethyl and triphenylmethylperoxy radicals, and (2) the heat of "sorption" for oxygen. For the "permeative–adsorption" type behavior suggested by our data the latter quantity should be very small. The former quantity will depend upon the similarities of the surroundings of the two radicals in the triphenylacetic acid matrix. The symmetric line shape observed for triphenylmethyl and triphenylmethylperoxy radicals is indicative of a radical with considerable freedom of motion. Esr spectra of peroxy radicals have been found to be very sensitive to orientation of the radical with respect to the direction of the magnetic field.[9e,12] In some orientations two peaks can be resolved due to the differences in *g* value as a function of angle. In a polycrystalline sample the signal due to peroxy radical would be expected to be broad and asymmetric if the radical were confined to a specific geometry. The signal observed, however, has the shape one would expect to find for the radical in solution where the radical is free to assume all orientations rapidly with respect to the direction of the magnetic field. The picture which evolves from these considerations is that triphenylmethylperoxy and probably triphenylmethyl radicals are trapped in a lattice hole with considerable freedom of motion. Thus the surroundings for both radicals in the solid lattice should be quite similar and the heats of sublimation should cancel in the over-all heat of reaction. We suggest, therefore, that the determined ΔH for the reaction of triphenylmethyl radical and oxygen should be applicable to the same reaction in solution or gas phase.[27]

Benson[28] has evaluated the standard heats of dissociation for alkyl, allyl, and benzylperoxy radicals in the gas phase from available data on the hydrogen dissociation energy for hydrogen peroxide and standard heats of formation for peroxides. For benzyl radical in the gas phase

$$C_6H_5CH_2\cdot + O_2 \rightleftarrows C_6H_5CH_2OO\cdot \qquad (24)$$

$\Delta H = -13$ kcal/mole. This value is close to the value found for triphenylmethyl radical but probably well outside our limit of error. Estimates for the difference in resonance energy between benzyl and triphenylmethyl radicals are 2–3 kcal.[29] Subtracting this amount from ΔH for benzyl radical gives $\Delta H = -10$–11 kcal for triphenylmethyl radical value, in satisfactory agreement with the 9 kcal observed.

Estimates of the equilibrium constant for eq 12 were also made for various radicals.[28] For benzyl radical the equilibrium constant for reaction 24 was given as 10^3 atm^{-1} at 27°. We calculate approximately 25 for this value for triphenylmethyl radical at this temperature. The ceiling temperature, defined as the temperature where $RO_2\cdot/R\cdot = 1$, was calculated to be 100° for benzyl radical at 0.1 atm of oxygen pressure. We calculate the ceiling temperature to be approximately 75° for triphenylmethyl radical at atmospheric oxygen pressure.

The effect of oxygen pressure on the equilibrium between triphenylmethylperoxy radical and triphenylmethyl radical and oxygen is not consistent with a Henry's law type behavior in which the oxygen activity in the solid varies linearly with oxygen pressure. Unfortunately, however, solubility data for gases in solids are extremely limited. The effect of oxygen pressure on the equilibrium is best discussed in terms of absorbed oxygen located throughout the entire solid lattice. The rapid complete conversion of triphenylmethyl radicals to triphenylmethylperoxy radicals upon exposure of irradiated triphenylacetic acid to air indicates that the solid is extremely permeable to oxygen and that the entire solid is accessible.

Estimated standard entropy changes for reactions of this type

$$RO_2\cdot \longrightarrow R\cdot + O_2 \qquad (25)$$

are close to 32 cal/mole °K for most alkyl radicals (30 for benzyl), but a lower value of 27.0 for an allyl radical was calculated.[28] It is possible from our data to evaluate a meaningful $\Delta S°$ for reaction 25 involving triphenylmethyl radicals.

Equation 11 defines the $(O_2)_{ads}$ concentration as the actual fraction of the available space in the solid matrix occupied by oxygen molecules. Our results indicate that, at atmospheric oxygen pressure, at which the equilibrium experiments were made, this fraction is essentially one. We have, therefore, used in our calculation of $\Delta H°$

$$K(\text{apparent}) = (Ph_3C\cdot)_s/(Ph_3COO\cdot)_s$$

whereas

$$K(\text{actual}) = [(Ph_3C\cdot)_s(O_2)_{ads}]/(Ph_3COO\cdot)_s$$

Since concentration units for the radical species will cancel, the assumption that the activity of the oxygen in the solid matrix is equal to that in the gas phase will allow the calculation of a thermochemically significant $\Delta S°$. At 298°K, K(apparent) = 0.10 (from Figure 5).

---

(27) The triphenylmethyl and triphenylmethylperoxy signals are admittedly somewhat asymmetric if formed on the surface (Figure 2). The difference in the observed ΔH (9.0 *vs.* 8.3 kcal/mole for radicals trapped internally and on the surface, respectively) is probably not significant, however, at this time.

With α-naphthyldiphenylmethylperoxy radical generated on the surface of α-naphthyldiphenylmethyl chloride a very asymmetric signal has been obtained. Here the radicals apparently are more confined to specific orientations with respect to the direction of the magnetic field. This may be due to the asymmetric nature of the aralkyl group and/or the geometric restrictions imposed by the surface of the particles on the radical. For this radical $\Delta H \simeq 9$ kcal/mole; preliminary results of Dr. Richard Kriens.

(28) S. W. Benson, *J. Am. Chem. Soc.*, **87**, 972 (1965).

(29) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

K(actual) = 0.02 atm. The standard free energy change is then $\Delta G° = 2300$ cal/mole and $\Delta S° = 23$ cal/mole deg.

Our preliminary estimate of 10.2 kcal/mole for the activation energy for the decomposition of triphenylperoxy radical to triphenylmethyl and oxygen is consistent with the observed value of 9 kcal/mole for the heat of decomposition for the triphenylperoxy radical. At this time the difference between these values may fall within the error of our determinations. However continued work is expected to improve these values.

Preliminary experiments with 9-phenylfluorene-9-carboxylic, diphenylacetic, 2,2-diphenylpropionic, and 2,2-diphenylbutyric acids have given esr spectra attributed to the hydrocarbon radical. Exposure to air has given the peroxy radical in the first two cases. Experiments with other stable free radicals, *e.g.*, tris(p-nitrophenyl)methyl radical, are in progress.

Oxygen-17 Nuclear Magnetic Resonance Studies of the Equilibria between the Enol Forms of β-Diketones

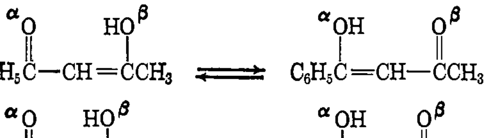
Malka Gorodetsky, Zeev Luz, and Yehuda Mazur

Contribution from the Organic Chemistry and Isotope Departments of the Weizmann Institute of Science, Rehovoth, Israel. *Received November 12, 1966*

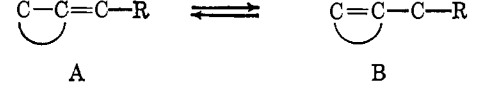
Abstract: A method for determining the relative concentrations of the two enol tautomers A and B of asymmetric β-diketones (eq 1a and b) using ^{17}O nmr spectroscopy is described. The ^{17}O spectra of eight ^{17}O-enriched asymmetric β-diketones were studied. Two sets of lines were observed: (a) one broad peak in the range −500 to −600 ppm (downfield from $H_2{}^{17}O$) due to the keto tautomer, and (b) two peaks in the range 0 to −500 ppm due to the two nonequivalent oxygens of the enol tautomers. From the chemical shift of the enol peaks the equilibrium constant, $K = [B]/[A]$, is calculated. The results show a small but systematic effect of ring size and substituents on K: (i) six-membered rings favor endocyclic double bonds while five-membered rings favor exocyclic double bonds; (ii) structure A is increasingly stabilized when R is changed from methyl to hydrogen to phenyl.

The equilibrium between keto and enol forms of β-diketones has been the subject of many extensive studies.[1–3] The most common method used to study this equilibrium is proton magnetic resonance spectroscopy (pmr).[4] Since the rate of the keto–enol interconversion is usually slow, separate signals of the protons due to the enol and keto forms may be observed and by intensity measurements the relative ratio of the two forms can be determined.

In a symmetrically substituted β-diketone (*e.g.*, acetylacetone) there is only one distinguishable enolic form. When the substituents on the β-diketone are not identical, two different enolic forms are possible, A and B.



$$C_6H_5\overset{\overset{\alpha}{O}}{\overset{\|}{C}}-CH=\overset{HO^{\beta}}{\overset{|}{C}}CH_3 \rightleftharpoons C_6H_5\overset{{}^{\alpha}OH}{\overset{|}{C}}=CH-\overset{O^{\beta}}{\overset{\|}{C}}CH_3 \qquad (1a)$$



(1b)

A B

In general the two forms will have different thermodynamic stabilities and the equilibrium constant

$$K = [B/[A] \qquad (2)$$

will be different from unity. The determination of this equilibrium constant is, however, impossible by classical chemical methods because the two enolic forms are in rapid dynamic equilibrium. Their interconversion involves merely an intramolecular proton transfer with a concomitant change in the electron distribution in the molecule. The rate of this proton transfer is fast even on the time scale of nuclear magnetic resonance frequency and therefore only one set of lines is displayed in the pmr spectra by the two enolic forms.[4] The rate of interconversion between the two enol forms is, however, slow on the time scale involved in ultraviolet[5] and infrared[6] spectroscopy. In fact ultraviolet measurements have been employed to determine K in a number of α-benzoyl ketones, but since the absorption maxima of the separate forms were not known, the results cannot be considered reliable.[5b] Another attempt to estimate K using a chemical method was based on the relative yield of formation of derivatives of one or the other tautomeric forms upon reaction with diazomethane.[7] The results depend, however, on the relative reaction rates of the two forms, which again are not known, and therefore this method cannot be used for quantitative calculations.

---

(1) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall Inc., Englewood Cliffs, N. J., 1964, pp 368–379.

(2) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Reinhart and Winston Inc., New York, N. Y., 1959, pp 376–384.

(3) G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Neuman, Ed., John Wiley and Sons, Inc., London 1956, pp 445–454.

(4) (a) H. S. Jarrett, L. S. Sadler, and J. N. Shoolery, *J. Chem. Phys.*, **21**, 2092 (1953); (b) N. Bhar, *Arkiv Kemi*, **10**, 223 (1957); (c) L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957); (d) L. W. Reeves and W. G. Schneider, *ibid.*, **36**, 793 (1958); (e) J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964).

(5) (a) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); (b) R. D. Campbell and H. M. Gillow, *J.Am. Chem. Soc.*, **82**, 5427 (1960).

(6) S. Forsen, F. Merenyi, and M. Nilsson, *Acta Chem. Scand.*, **18**, 1208 (1964).

(7) E. D. Campbell and H. M. Gillow, *J. Am. Chem. Soc.*, **84**, 1440 (1962).