

ELECTRON PARAMAGNETIC RESONANCE STUDIES
ON THE PRODUCTION OF FREE RADICALS IN
HYDROGEN PEROXIDE AT LIQUID NITROGEN
TEMPERATURE¹

Sir:

Since the first e.p.r. observation by Ingram² and his colleagues on the photolytic formation of free radicals in hydrogen peroxide at liquid nitrogen temperature, a considerable amount of research has been done on the identification of paramagnetic species produced under these or similar conditions.

Preparation of the samples for e.p.r. examination has been performed either by condensation at liquid nitrogen temperature of the products of electric discharge in various gaseous mixtures containing H₂O₂ vapor^{3,4} or by direct photolysis of aqueous H₂O₂ solutions frozen in liquid nitrogen.^{2,5,6} In all the cases reported, the e.p.r. spectrum seems to represent the same species, believed by most authors to be the HO₂ radical. However, Kaitmazov and Prokhorov⁵ indicate that: (1) ultraviolet irradiation (with $\lambda > 2600 \text{ \AA.}$) of H₂O₂ may result only in the breakage of the HO-OH bond, and (2) no secondary reactions occur during photolysis, since the change of H₂O₂ concentration in the range from 5-98% does not affect the spectrum. Thus, according to Kaitmazov and Prokhorov, the e.p.r. spectrum obtained by H₂O₂ photolysis at liquid nitrogen temperature must be derived from OH radicals. The present report summarizes the results of e.p.r. experiments carried out with H₂O₂ solutions irradiated by T β -particles and ultraviolet light at liquid nitrogen temperature

Irradiation by T β -Particles.—6 M H₂O₂ solution was tritiated with T₂O to an activity of 0.3 c./ml. and frozen in glass sample tubes in liquid nitrogen. Tritium has been chosen as an internal source of radiation since, as reported previously,⁷ it allows one to avoid the background of irradiated glass in the e.p.r. spectrum. The resulting e.p.r. spectrum (Varian V4500, X-band e.p.r. spectrometer) shown in Fig. 1A, is very similar to the spectra reported^{5,6} for H₂O₂ irradiated by ultraviolet light and consists essentially of a fairly broad band, poorly resolved into two peaks, with separation of about 12 gauss. This spectrum is, however, distinctly different from that usually attributed to OH radicals and obtained by irradiation with Co⁶⁰ γ -rays⁸ or T β -particles⁷ of pure H₂O ice.

The e.p.r. spectrum produced by T β -particles in H₂O ice at liquid nitrogen temperature is shown in Fig. 1B. Apart from their spectral appearance, radicals A (produced in H₂O₂) and B (in H₂O) differ markedly in thermal stabilities. As shown in Fig.

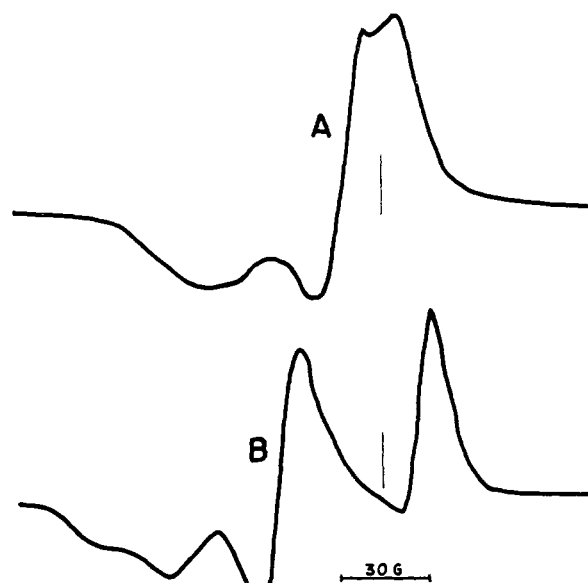


Fig. 1.—E.p.r. spectra (derivative curves) of radicals produced by T β -particles at liquid nitrogen temperature in 6 M H₂O₂ (A) and H₂O (B): Vertical lines indicate the position of DPPH signal. The field increases to the right. (A) is thought to be due to HO₂ and (B) to OH.

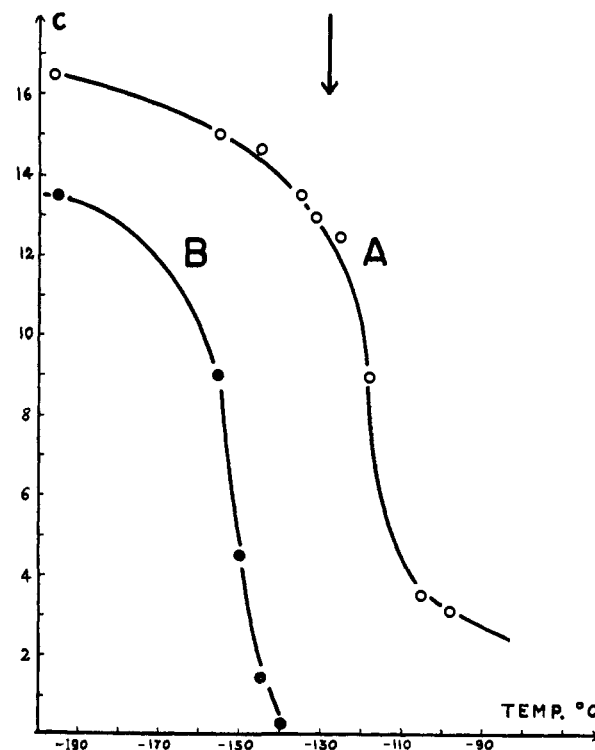


Fig. 2.—Decay of radicals A and B on warming: the experiment was carried out by "pulse" warming, *i.e.*, by alternate keeping of the sample at a given temperature for about 5 minutes and then recording the spectrum at liquid nitrogen temperature. The ordinate axis, scaled in relative units, expresses the concentration C of free radicals.

2, radicals A disappear on warming at a temperature that is about 30° higher than for radicals B. The arrow in Fig. 2 indicates the temperature re-

(1) Supported by a grant from the National Research Council of Canada.

(2) D. J. E. Ingram, W. G. Hodgson, C. A. Parker and W. T. Foex, *Nature*, **176**, 1227 (1953).

(3) R. Livingston, J. Ghorncley and H. Zeldes, *J. Chem. Phys.*, **24**, 483 (1956).

(4) R. J. Gorbanev, S. D. Kaitmazov, A. M. Prokhorov and A. B. Tsentsiper, *Zhur. Fiz. Kim.*, **31**, 515 (1957).

(5) S. E. Kaitmazov and A. M. Prokhorov, *J. Exp. Theoret. Phys. (USSR)*, **36**, 237 (1960).

(6) R. C. Smith and S. J. Wyard, *Nature*, **186**, 226 (1960).

(7) J. Kroh, B. C. Green and J. W. T. Spinks, *Nature*, **189**, 655 (1961).

(8) S. Siegel, L. H. Baum, S. Skolnik and J. M. Flournoy, *J. Chem. Phys.*, **32**, 1219 (1960).

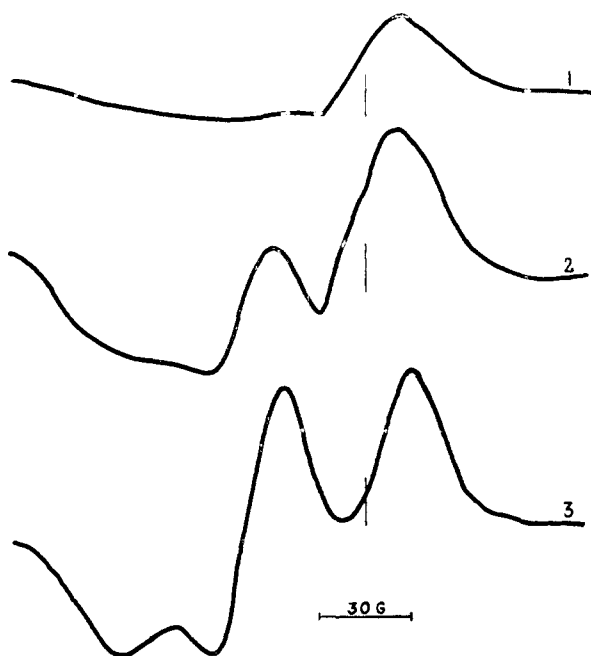
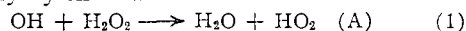


Fig. 3.—Successive stages of e.p.r. spectrum of 10^{-3} M H_2O_2 irradiated with ultraviolet lamp for (1) 30 min., (2) 2 hours, and (3) 12 hours.

ported by Siegel⁸ and his colleagues for the beginning of measurable decay of the spectrum considered by him as possibly representing HO_2 radicals. Finally, the saturation concentration of radicals B produced in H_2O ice by T β -particles, applied at a dose rate of 7.6×10^{17} ev./ml. hr. is of the order of 10^{18} spins/ml., whereas the concentration of radicals A, produced in tritiated 6 M H_2O_2 , easily exceeds this value, and for a dose rate of 2.51×10^{17} ev./ml. hr. and a total dose of 2.5×10^{20} ev./ml. approaches 10^{19} spins/ml. Under these conditions the yield of radicals A seems to be higher than that of radicals B by a factor of the order of 10.

Assuming that the primary results of H_2O_2 photolysis are limited to the production of OH radicals, probably represented by spectrum B in Fig. 1, our further experiments were based on the assumption that radical A is produced in H_2O_2 by a secondary process involving OH radicals, most likely by the reaction



Consequently, the influence of H_2O_2 concentration on e.p.r. spectra was investigated.

Photolysis by Ultraviolet Light.—Aqueous H_2O_2 solutions of concentrations ranging from 10^{-3} to 10 M were irradiated in quartz tubes at liquid nitrogen temperature by ultraviolet light (Mineralight Model SL without filter). Varying the concentration of H_2O_2 in the range 10 to 10^{-2} M does not seem to affect the e.p.r. spectrum, which, in all cases, remains identical with spectrum A in Fig. 1. However, on approaching a concentration of the order of 10^{-3} M the spectrum, especially after longer ultraviolet irradiation, changes, as shown in Fig. 3.

Finally, after a long irradiation, the spectrum becomes identical with that in Fig. 1B, believed to represent OH radicals.

Characteristically, even for dilute H_2O_2 solutions, the initial spectrum recorded after short ultraviolet irradiation seems to represent mainly radical A and in course of further irradiation (Fig. 3) is gradually replaced by B. This change of spectrum probably results from the progressive decomposition of H_2O_2 . Thus, as the photolysis proceeds, the number of OH radicals escaping reaction (1) increases.

The doublet spectrum obtained after prolonged irradiation disappears on warming according to curve B in Fig. 2. After reaching the temperature of about -130° , only a weak signal, corresponding to the spectrum of radical A, is left. The concentration of the latter may be estimated as about 10% of the initial concentration of radicals represented by the doublet.

In view of the above facts, we are inclined to believe that the e.p.r. spectra reported hitherto for concentrated (2–98%) solutions of H_2O_2 , irradiated by ultraviolet light at liquid nitrogen temperature, represent mainly HO_2 radicals in reaction (1). OH radicals produced in the primary photolytic process may be observed only in dilute (10^{-3} to 10^{-2} M) H_2O_2 solutions when the occurrence of reaction (1) is limited and a large fraction of OH radicals remains unscavenged by hydrogen peroxide.

CHEMISTRY DEPARTMENT
UNIVERSITY OF SASKATCHEWAN
SASKATOON, CANADA

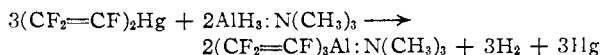
JERZY KROH
BASIL C. GREEN
JOHN W. T. SPINKS

RECEIVED FEBRUARY 25, 1961

A PERFLUOROVINYALUMINUM COMPOUND

Sir:

The preparation of some perfluorovinylboron compounds was reported recently,¹ and a communication also has appeared in print on a perfluoromethylboron derivative.² In our laboratory we have been able to synthesize a perfluorovinylaluminum compound. This has been accomplished by a method which has been found to be of general utility in the preparation of organoaluminum compounds³



To 0.99 g. (0.011 mole) of aluminum hydride trinethylamine⁴ in ethyl ether was added slowly, under stirring, 6.0 g. (0.017 mole) of bis(perfluorovinyl)-mercury,⁵ likewise dissolved in ethyl ether. A vigorous reaction occurred even at -20° and hydrogen was liberated immediately. After the addition was complete, stirring was continued for 12 hr. at room temperature and then another 0.50 g. (0.0014 mole) of $(\text{CF}_2=\text{CF})_2\text{Hg}$

(1) S. L. Stafford and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6238 (1960).

(2) T. D. Parsons, E. D. Baker, A. B. Burg and G. L. Juvinall, *ibid.*, **83**, 250 (1961).

(3) B. Bartocha, A. J. Bilbo, D. E. Bublitz and M. Y. Gray, *Angew. Chem.*, **72**, 36 (1960).

(4) J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960).

(5) R. N. Sterlin, Li-Vei-Gan and I. L. Knunyants, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 1506 (1959) [*C.A.*, **54**, 1273e (1960)].