The Dipole Moments of Fluorenone Peroxide and Bishydroperoxide

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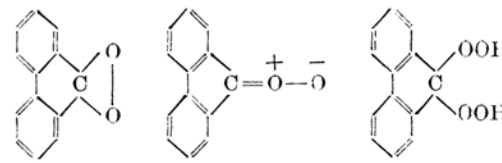
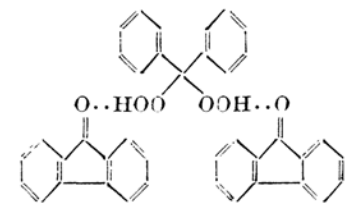
In 1940, Wittig and Pieper[1] prepared a new monomeric peroxide, viz., the so-called "fluorenone peroxide"[1] and discussed its structure. They regarded the formula (I) as unsatisfactory, because the yellow color of the crystal seemed to reveal a ketonic double bond. And they favored the oxo-öxide structure (II) instead, which appeared to agree with many of its properties, including its solubilities.

In 1942, Prof. Murakami, of Osaka University, offered me this substance prepared by the Wittig and Pieper's method and we measured its dipole moment in benzene at room temperature. It was then evident from the observed value of its moment, viz., 3.1D that the ring structure (I) which has a smaller moment than 2D should be ruled out. Further, the oxo-öxide structure which corresponds to a large moment of about 6D could not represent the actual state of the molecule. In the preceding article[2] it was suggested, therefore, that resonance occurs among various structures including (II), resulting in a lesser moment.



(I) (II) (III)



(IV)

(1) G. Wittig und G. Pieper, *Ber.*, **73**, 295 (1940).

(2) K. Higasi, *Bull. I. P. C. R. Tokyo*, **21**, 1147 (1942).

In 1949, Criegee, Schnorrenberg and Beck[3] reported that Wittig's "fluorenone peroxide" is not a simple substance but a mixture of two molecules of fluorenone and one molecule of its bishydroperoxide (III). In benzene solution this molecular compound (IV) dissociates into the three components, giving a monomeric value in the molecular weight determination.

In the present note I wish to report the result of a reexamination of our data from the view-point of Criegee and his pupils. From the apparent polarization of "fluorenone peroxide", the total polarization of the molecular compound (in a dissociated state) was calculated, and then by subtracting the polarizations of two fluorenone molecules,[4] the polarization of the bishydroperoxide (III) was obtained. The dipole moment thus evaluated for the latter substance was 2.4D* in benzene (with fluorenone).

The polarity of the bishydroperoxide (III) arises chiefly from the two C—O dipoles and two O—H dipoles. Besides these, there are small moments induced in the hydrocarbon residue, but a correction for them may be included in the resultant moment for C—O dipoles, which are in a fixed position to the plane of rings. In contrast to these, the two O—H dipoles can rotate around two axes of rotation, viz., the C—O, and O—O linkages (Fig. 1). As a first approximation we may regard the polarity of the molecule as consisting of three independently rotating dipoles, viz., one for O-C-O dipole of 1.0D, and the other two of 1.53D each for the O—H groups.[5] This rough picture was in fact in good accord with the observed moment, giving 2.38D as the calculated moment.**

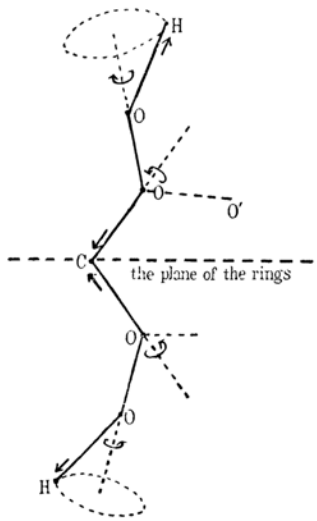


Fig. 1.—The axes of rotation in bishydroperoxide

Further, it is of interest to find that the apparent polarization of fluorenone peroxide increases with the increase in concentration, and that the bishydroperoxide reveals the same tendency but that it is even more pronounced. In Fig. 2 the molecular polarization of the bishydroperoxide was plotted against the mole fraction of the solute and compared with the curve for fluorenone itself.

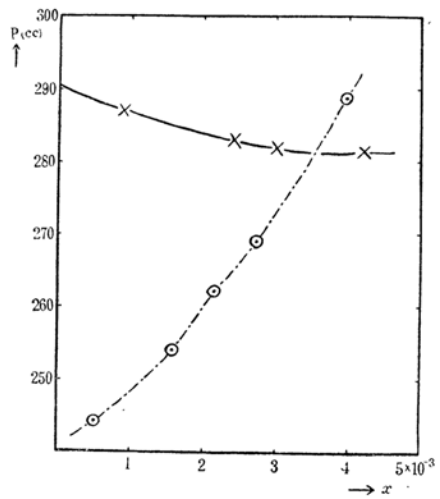


Fig. 2.—Molecular polarization in benzene solution at 25°C (P) and mole fraction (x).
× Fluorenone (Le Fèvre et al[4])
⊙ Bishydroperoxide (Higasi, the sample B*)

The increase in polarization with increasing concentration may be accounted for by making any of the following two assumptions. First, we regard it as characteristic of the solute with O—H group, e.g., the polarizations of alcohols in hexane. Secondly, the bishydroperoxide has a strong tendency to interact with one or two molecules of fluorenone, thus forming very polar complexes. The latter interpretation may be the more plausible,

(3) R. Criegee, W. Schnorrenberg and J. Beck, *Ann.*, **565**, 7 (1949).

(4) E. D. Hughes, C. G. Le Fèvre, R. J. W. Le Fèvre, *J. Chem. Soc.*, 207 (1937).

* The sample A (m. p. 107°~8°) gave 3.1D for fluorenone peroxide and 2.4 D for the bishydroperoxide, while the sample B (m. p. 104°) gave 3.2 D and 2.9 D, respectively. The sample A was recrystallized from B (Cf. Wittig and Pieper: m. p. 108°).

(5) C. P. Smyth, *J. Phys. Chem.* **41**, 209 (1937); and other papers.

** The moment of the bishydroperoxide m is calculated as $m^2=1\times1.0^2+2\times1.53^2$.

because the chance for the association in this type is twice that in the former.

In conclusion, it may be safely stated that a better explanation of our dielectric measurement can be obtained from the work of Criegee and his school than from that of Wittig and Pieper.

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