The Electron Spin Resonance Absorption of Molecular Addition Compounds

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(Received September 12, 1960)

Recently, a number of molecular complexes formed between electron donors and acceptors have been investigated by the method of electron spin resonance (ESR) and also by the measurement of electrical conductivity$^{1-3)}$. On the molecular complexes formed between phenylene diamines and halogenated quinones, Bijl, Kainer and Rose-Innes$^{3)}$ and also Matsunaga and McDowell$^{4)}$ reported the existence of unpaired electrons in those complexes. However, it has been found that the observed intensity of ESR absorption fluctuate from specimen to specimen.

In this report, we present the electron spin resonance absorption of the molecular complexes, formed between dimethyl-aniline (I, DMA; liquid) and halogenated benzoquinones (II, *x*-anils) and of those between also tetramethyl-*p*-phenylene diamine (III, TMPD) and *x*-anils as a function of time.

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1) D. D. Eley and H. Inokuchi, Proc. Third Carbon Conf., 91 (1959).

2) D. D. Eley, H. Inokuchi and M. Willis, *Discussions Faraday Soc.*, **28**, 54 (1959).

3) D. Bijl, H. Kainer and A. C. Rose-Innes, *J. Chem. Phys.*, **30**, 765 (1959).

4) Y. Matsunaga and C. A. McDowell, *Nature*, **185**, 916 (1960).

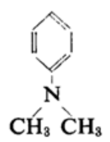
TABLE I. THE PARAMAGNETIC PROPERTIES OF MOLECULAR COMPLEXES FORMED BETWEEN PHENYLENE DIAMINE AND HALOGENATED QUINONES

Donor	DMA			TMPD		
Acceptor	chloranil	bromanil	iodoanil	chloranil	bromanil	iodoanil
Color	blue violet	black violet	black violet	black	brownish black	brownish black
g-value	2.0003 ± 0.0004	2.0071 ± 0.0005	2.0000 ± 0.0004	2.0036 ± 0.0004	2.0043 ± 0.0004	2.0037 ± 0.0004
Line width (gauss)	20	4 (*) 32 (†)	22	7	13 (*) 40 (†)	22
Spin population (**)	~0.01%	5%	17%	5%	7%	10%

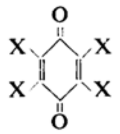
* Observed with freshly prepared specimen.

† Observed with specimen left for 40 days in air.

** Maximum value.

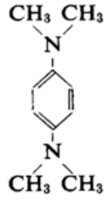


(I)



X=Cl, Br, I

(II)



(III)

These complexes were made as follows: 50 mg. of purified x-anil were dissolved in 5 cc. of DMA, and one-fifth of its volume of ethanol was added into the solution to precipitate the deep colored molecular complex. After filtration, crystals of the complex were sealed up immediately into glass tubings (diameter 2 mm.) under an atmosphere of argon or oxygen. In the case of TMPD-x-anil complexes, the solutions of TMPD and of x-anil in benzene were mixed with each other to produce the precipitate of the complex. The precipitate was filtered and washed with a small amount of benzene and of ether successively. These complexes were also kept in glass tubings to prevent a decomposition of TMPD by humidity.

The electron spin resonance absorption spectra of these complexes were observed in association with x-band microwave spectrometer, Hitachi MPS-1. The spin concentrations in these complexes were measured in comparison with a standard piece of α,α'-diphenyl-β-picrylhydrazyl or 'violanthrone'*. The g-values of these complexes possessed near 2.0 and was estimated from the value of ultramarine which is 2.028.

As illustrated in Table I, it was found that DMA-x-anil complexes, for which Bijl et al.[3] observed no ESR signals possess definite ESR absorption around $g=2.0$. This fluctuation of intensity of ESR absorption may depend upon preparation techniques of these complexes. The study of g-values of DMA-chloranil and also of DMA-iodoanil, which are fairly smaller than the value of free electron itself ($g=2.0023$), is a noteworthy problem.

In the case of TMPD-x-anil molecular complexes (Table I), the spin concentrations changed strongly with great regard to the time after preparation as shown in Fig. 1 for TMPD-bromanil. However, the atmospheric gases surrounding the complexes were not so sensitive to the spin concentration of the complexes excepting TMPD-chloranil.

The ESR absorption curve of TMPD-bromanil complex also changed violently with time in its shape. At first, two ESR absorption peaks, their g-values were 2.0030 and 2.0043 respectively, were observed for freshly prepared specimen (curve A of Fig. 2). After a couple of days, a new absorption peak appeared (curve B). However, during a next few days, two of them disappeared and only one ESR absorption peak having $g=2.0043\pm0.0004$ remained (curve C). Through a long period observation, the line width of the

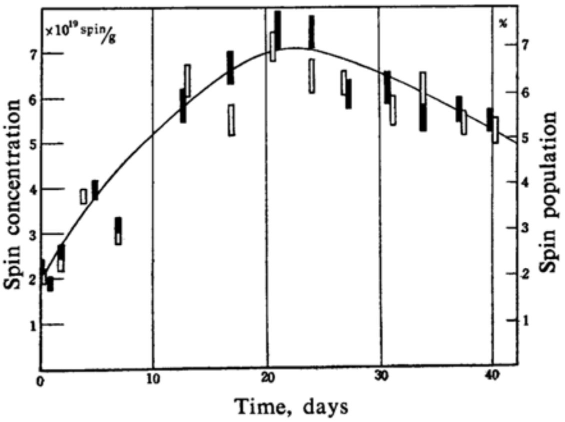


Fig. 1. The time dependence of spin population of tetramethyl-p-phenylene diamine-bromanil complex.

■ in air, □ in argon

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* Crude violanthrone comprises a small amount of free radicals. This compound can be applied as a substandard piece for the estimation of spin concentration because the free radical is stabilized in the matrix, violanthrone.

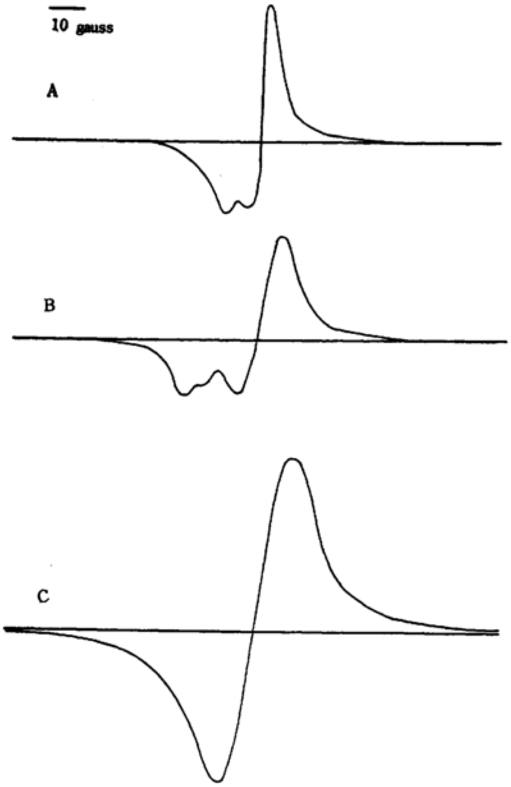

Fig. 2. The derivative curves of electron spin resonance absorption of tetramethyl-*p*-phenylene diamine-bromanil complex in air: (A) for fresh specimen, (B) and (C) for specimen which is exposed in air for 2 days and also for 4 days respectively.

absorption curve was spread from 12∼13 gauss to 50 gauss (120 days after preparation).

It seems likely that these changes of spin concentrations and also line widths with time are introduced from the progress of complex formation and/or decomposition of these addition compounds.

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