# Conductance of Picric Acid and Diisopropylamine in Isopropanol, Methyl Ethyl Ketone, and in an Isopropanol-Ketone Mixture

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Picric acid. In the concentration range $10^{-4} - 5 \times 10^{-3}$ M of picric acid in isopropanol, and in a mixture of 50 % isopropanol and 50 % methyl ethyl ketone, simple dissociation of the acid:

$$HPi \rightleftharpoons H^+ + Pi^- \qquad (1)$$
$$\text{diss.const.} = K_1$$
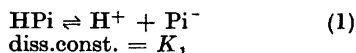
predominates if the Kraus-Bray plot of the Ostwald dilution function results in a straight line. This plot of $1/\Lambda_c$ *versus* $c \cdot \Lambda_c$ has the intercept $1/\Lambda_{01}$, and the slope $1/K_1 \cdot \Lambda_{01}{}^2$, where Λ_c is the equivalent conductance at the concentration c, and Λ_{01} that at infinite dilution.

The specific conductivity of the picric acid solutions was measured and the equivalent conductance was calculated, see Table 1. The Kraus-Bray plot yielded a straight line for these two solvents which proved that eqn. (1) is valid. Λ_{01} and K_1 were evaluated, see Table 2.

The Ostwald dilution function applied to picric acid in methyl ethyl ketone was not linear, which indicated that the dissociation was more complicated. French and Roe [1] have assumed both ion pair association and triple ion formation in acetone and acetophenone according to eqn. (1) and to

$$Pi - H - Pi^- \rightleftharpoons HPi + Pi^- \qquad (2)$$
$$\text{diss.const.} = K_2$$
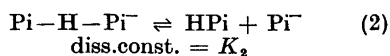
The conditions for a dissociation scheme of the type given above were satisfied by picric acid in methyl ethyl ketone. It was namely found that the slope of $\log \Lambda_c$ *versus* $\log c$ was -0.7, that $\Lambda_c \cdot c^{\frac{1}{2}}$ *versus* c was non-linear, and that the numerical value of the slope increased for more concentrated solutions.

French and Roe [1] developed the following conductance equation based on the theory of triple ion formation.

Table 1. Equivalent conductance of picric acid at 25.0°C.

Isopropanol		Methyl ethyl ketone		50 % Isopropanol 50 % Methyl ethyl ketone	
Conc. $\times 10^3$	Eq.cond.	Conc. $\times 10^3$	Eq.cond.	Conc. $\times 10^2$	Eq.cond.
4.787	5.08	3.377	0.462	9.330	1.20
2.394	6.68	1.689	0.793	4.665	1.68
1.197	8.69	0.8445	1.34	2.333	2.32
0.5985	11.3	0.4223	2.22	1.166	3.21
0.2993	14.2	—	—	0.5830	4.33
0.1497	17.5	—	—	0.2915	6.04
—	—	—	—	0.1458	8.28

Table 2. Dissociation constants and limiting equivalent conductance of picric acid at 25.0°C.
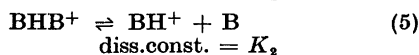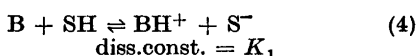
Solvent	Λ_{01}	K_1	K_2
Isopropanol	24	2.5×10^{-4}	
Methyl ethyl ketone	148	6.4×10^{-9}	7.1×10^{-3}
50 % Isopropanol 50 % Methyl ethyl ketone	25	2.3×10^{-4}	

$$\Lambda_c[c(K_2 + c)]^{1/2} = \Lambda_{01}(K_1 K_2)^{1/2} + \Lambda_{03}c(K_1/K_2)^{1/2} \quad (3)$$

where $\begin{cases} \Lambda_{02} = \Lambda_{OH^+} + \Lambda_{OPi^-} \\ \Lambda_{03} = \Lambda_{OH^+} + \Lambda_{OPi-H-Pi^-} \end{cases}$

K_1 and K_2 (Table 2) were evaluated from the intercept and from the slope of the linear plot of $\Lambda_c[c(K_2 + c)]^{1/2}$ *versus* c (Fig. 1). Λ_{01} was calculated by Waldens rule, and $\Lambda_{03}/\Lambda_{01}$ was set to 1/3.

Diisopropylamine. The behaviour of di-isopropylamine can be accounted for by two different ionization equilibria in iso-propanol, methyl ethyl ketone and in the mixture.

$$B + SH \rightleftharpoons BH^+ + S^- \quad (4)$$
$$\text{diss.const.} = K_1$$

$$BHB^+ \rightleftharpoons BH^+ + B \quad (5)$$
$$\text{diss.const.} = K_2$$

The equivalent conductance values are presented in Table 3. The conductance equation (3) where

$\begin{cases} \Lambda_{01} = \Lambda_{0BH^+} + \Lambda_{0S^-} \\ \Lambda_{03} = \Lambda_{0BHB^+} + \Lambda_{0S^-} \end{cases}$

explained the experimental results. $d(\log \Lambda)/d \log c$ was -0.7, the $\Lambda c^{\frac{1}{2}}$ *versus*
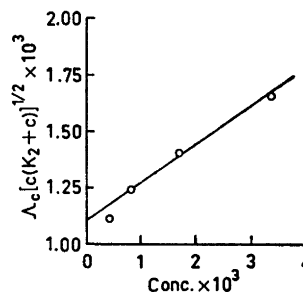

Fig. 1. Application of eqn. (3) to the system picric acid-methyl ethyl ketone.

c plot was nonlinear and had a negative slope. The plot of $\Lambda_c[c(K_2 + c)]^{\frac{1}{2}}$ *versus* c was linear (Fig. 2). The results are given in Table 4.

Experimental. Methyl ethyl ketone, for chromatography, was shaken with $CaSO_4$ and distilled. Isopropanol, *pro analysi*, was used without further purification. The water content was 0.06 %. In a mixture of the solvents the amount of water increased gradually

Table 3. Equivalent conductance of diisopropylamine at 25.0°C.

Isopropanol		Methyl ethyl ketone		50 % Isopropanol 50 % Methyl ethyl ketone	
Conc. × 10²	Eq.cond.× 10²	Conc. × 10²	Eq.cond. × 10²	Conc. × 10²	Eq.cond. × 10
3.545	0.846	3.578	1.31	3.570	0.535
1.773	1.30	1.789	2.07	1.785	0.992
0.8865	1.92	0.8945	3.24	0.8925	1.84
0.4433	3.4	0.4473	5.37	0.4462	3.25
0.2217 *	4.3	0.2237 *	9.4	0.2231	5.24

* Solvent corrections > 50 %.

Table 4. Dissociation constants and limiting equivalent conductance of diisopropylamine at 25.0°C.

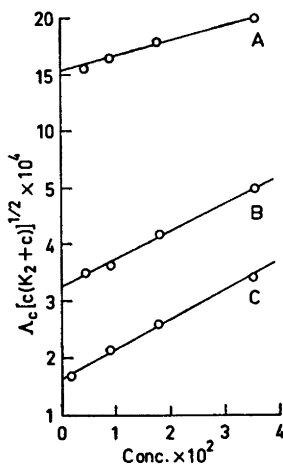| Solvent	Λ_{01}	K_1	K_2
Isopropanol	35	3.1×10^{-9}	6.8×10^{-3}
Methyl ethyl ketone	198	1.7×10^{-10}	1.7×10^{-2}
50 % Isopropanol 50 % Methyl ethyl ketone	59	2.6×10^{-8}	3.6×10^{-2}

Fig. 2. Application of eqn. (3) to the system: A, diisopropylamine-50 % isopropanol-50 % methyl ethyl ketone; B, diisopropylamine-methyl ethyl ketone; C, diisopropylamine-isopropanol.

because of acetal formation, and therefore freshly prepared solutions were used throughout.

The conductometric measurements were made at a frequency of 300 Hz using a circuit containing operational amplifiers. The accuracy of the bridge was within ± 0.1 % for $\varkappa > 10^{-5}$ ohm^{-1} cm^{-1} and within ± 1 % for $\varkappa > 5 \times 10^{-7}$ ohm^{-1} cm^{-1}. A conductivity cell suitable for nonaqueous solutions was made. The electrodes, placed at a distance of 0.4 cm and with an area of 3 cm^2 each were black platinized. All measurements were carried out at 25.0°C. The conductivity of pure isopropanol was 9×10^{-8}, of methyl ethyl ketone 1.5×10^{-7} and of the mixture 2.6×10^{-7} ohm^{-1} cm^{-1}. The same solvent corrections were subtracted throughout.

1. French, C. M. and Roe, I. G. *Trans. Faraday Soc.* **49** (1953) 314.

Decay of Radiation Induced Radicals and the Yield of Thermoluminescence

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The loss of biological activity of compounds exposed to ionizing radiation in the dry state is in part the end result of the secondary processes occurring after absorption of the radiation energy. Electron spin resonance (ESR) spectroscopy and thermoluminescence (TL) measurements have found increasing use in the study of these secondary processes. TL studies involve measurements of the light emitted from irradiated compounds upon subsequent heat-treatment. Since heat-treatment facilitates the decay of radiation-induced radicals, it seems of interest to study whether the yield of TL is somehow related to the concomitant disappearance of radicals, as measured by ESR spectroscopy. It is the purpose of the present communication to present an empirical relationship between results obtained with TL and ESR spectroscopy.

When substances are irradiated in the dry state at cryogenic temperatures and subsequent heat-treated, part of the radicals observable at low temperature will disappear in combination reactions (see, *e.g.*, Zimmer and Müller [1]). When attempts were made to plot our results on the extent of radical decay upon heat-treatment after irradiation at 77°K against the TL yield observed by Lehman and Wallace [2] on the same compounds, no obvious relationship was found. However, when the disappearance of ESR centers was plotted *versus* the product of the yield of TL and of ESR centers at 77°K, a straight line in a logarithmic plot, as shown in Fig. 1 A, was obtained.

The number of radicals observed by ESR spectroscopy after irradiation with increasing doses will initially increase linearly with the dose. At higher doses, however, the apparent rate of radical formation will decrease, and eventually the number of ESR centers in the sample will reach a limiting, maximum number.[3-6] In Fig. 1 B