

NOTES

Note on the Titration of *p*-Hydroxybenzoic Acid

BY ARTHUR OSOL AND MARTIN KILPATRICK

In a study of the solubility of the hydroxybenzoic acids in aqueous salt solutions¹ we determined the amount of acid present in the solution by titration with sodium hydroxide using phenolphthalein as indicator. Although earlier workers had not succeeded in obtaining satisfactory results in the titration of the para acid using phenolphthalein, we discovered that in the presence of larger amounts of the indicator a faint pink color could be detected in bright light which gave results of moderate accuracy.

In a private communication I. M. Kolthoff states that phenolphthalein is unsatisfactory as an indicator in that the end-point is vague and that the results are two to three per cent. high. He recommends the use of brom thymol blue as indicator, the end-point being matched with a buffer of *pH* 6.8. As we subsequently found brom thymol blue to be a better indicator, we considered it advisable to repeat the determinations of the solubility of *p*-hydroxybenzoic acid in aqueous potassium chloride solutions. The results of the new determinations are given in Table I.

TABLE I

SOLUBILITIES OF *p*-HYDROXYBENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONSSolutions 0.01 molar in sodium salt. Correction, -0.0002

KCl, moles per liter	Total acid, mole per liter	Molecular acid, mole per liter	"Salting-out" constant
0	0.0445	0.0434 ^a	..
0.2	.0417	.0413	0.098
.5	.0391	.0387	.096
.7	.0374	.0370	.096
1.0	.0351	.0347	.095
1.5	.0315	.0311	.095
2.0	.0282	.0279	.095
2.5	.0254	.0251	.094

^a In calculating the "salting-out" constants this solubility was taken to be 0.0432, the figure obtained by applying the method of least squares to all of the solubilities.

A comparison of the solubilities given above with those obtained when using phenolphthalein as indicator shows the latter to be higher to the extent reported by Kolthoff. However, the individual "salting-out" constants are approximately the same as those given in our first paper,

(1) Osol and Kilpatrick, *THIS JOURNAL*, **55**, 4440 (1933).

while the average constant for the new solubilities, as determined by the method of least squares, is the same as that previously reported, namely, 0.095.

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The Induction Period in the Oxidation of Propane

BY WENDELL P. MUNRO

The reaction of propane with oxygen in the Pyrex bulb of a static apparatus shows, as does that of other paraffin hydrocarbons, a long induction period followed by a rapid reaction. The latter was found unsuited for study both because it was too rapid to permit precise measurement and because the heat evolved caused the mixture to depart widely from the desired isothermal condition.

The induction period, which involved no observable pressure change, was found to be fairly reproducible, and was taken to be the time for an intermediate to build up to a critical concentration. Actually, the time up to 5% of the final pressure increase was taken as a convenient measure; it differs only slightly from the time of first observable pressure change and can be more precisely determined. With propane in excess (3.81:1 and 1:1 mixtures) at a total pressure of 7-800 mm. the reaction occurred at temperatures from 245° upward; the temperature coefficient (slope of the $\ln_e t_{\min.}$ vs. $1/T_{\text{abs.}}$ curve) was 2.0×10^4 . When the partial pressure of oxygen was increased (1:5 mixture) at the same total pressure, the lowest temperature at which reaction could be observed was raised to 306°, and the temperature coefficient nearly doubled (3.9×10^4). When propane was in excess the reaction "ran away" on several occasions; increasing the partial pressure of oxygen suppressed this tendency completely. In fact, runs were made at temperatures 60° above that at which the reaction was almost instantaneous without any departure from the usual smooth pressure rise.

Lowering the total pressure lowered the tem-