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 solutions[1] 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 *p*H 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 Solutions

Solutions 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, 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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(1) Osol and Kilpatrick, This Journal, **55**, 4440 (1933).

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 $\ln_e t_{\text{min.}}$ *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 temperature coefficient, the effect being especially pronounced for 1:5 mixtures. At 200 mm. the temperature coefficient for the 1:1 mixture was 1.6×10^4, the lowest reaction temperature 286°. At 300 mm. the temperature coefficient for the 1:5 mixture was only 1.0×10^4, and the lowest reaction temperature 345°.

A reasonable explanation would be that, as the pressure is lowered, a surface reaction becomes predominant over a gas phase reaction. To test this, runs were made with a bulb packed with bits of broken Pyrex. However, at 600 mm. with a 1:5 mixture, the reaction was found to have the high temperature coefficient 3.5×10^4. This does not deny the above hypothesis, for at the same time the lowest reaction temperature was raised to 403°, so that even though the surface had been increased many-fold the homogeneous reaction with its higher temperature coefficient could still be predominant.

When runs were made in an empty bulb, the walls of which had been coated with potassium chloride, the pressure rose gradually from the very beginning of each experiment. For this reason one cannot compare the 5% times of these runs with those of the previous sets. Nevertheless, judging from the temperature range over which the reaction could be observed, a high temperature coefficient probably obtained here also. The lowest temperature of reaction was 289° for a 1:1 mixture at 700 mm. Thus the potassium chloride coating inhibits the reaction at low, but not at high temperatures.

It was interesting to note in several instances during this work the appearance of several consecutive rapid reactions after a long induction period, just as was reported by Thompson and Kelland [*J. Chem. Soc.*, 1809 (1931)] in the case of the oxidation of hydrogen sulfide.

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The Behavior of Unsaturated Hydrocarbons toward the Grignard Reagent at Elevated Temperatures

BY CORLISS R. KINNEY AND ROBERT G. LARSEN

Occasionally assumptions have been made that Grignard reagents add to ethylenic or acetylenic linkages. These assumptions have been most conclusively refuted by Gilman and co-workers.[1] In addition they have made several exhaustive studies of the behavior of the Grignard reagent toward ethylenic and acetylenic hydrocarbons, over thirty hydrocarbons being included.[2] Several additional hydrocarbons have been studied by Wieland and Krause,[3] and by Wilson and Hyslop.[4] In all of this work no reaction was observed to take place between reagent and unsaturated hydrocarbon. These experiments, however, were carried out at temperatures not exceeding the boiling point of the ether solutions of the reagents; consequently, we have extended the work to higher temperatures to determine whether the reaction might be induced under such conditions.

Gilman and associates[2a,b,c] proved that ethylmagnesium bromide failed to react with the unsaturated hydrocarbons by showing that just as much ethane was liberated, by treatment with water, from aliquot portions of the reagent after contact with the hydrocarbon as before. This method is unsuited for use at higher temperatures because the reagent will decompose if heated too strongly. Therefore, phenylmagnesium bromide and several unsaturated hydrocarbons were chosen which would yield crystalline products if a reaction took place.

The phenylmagnesium bromide was prepared in the usual way in ether solution and in a four to one ratio to the hydrocarbon which was to be added. The hydrocarbon was dissolved in one of several higher boiling solvents; xylene, diphenyl, diphenyl ether and a fraction of kerosene, all were used. The resulting solution was added to the Grignard reagent and the mixture distilled until the

[1] (a) Gilman and Heckert, THIS JOURNAL, **42**, 1010 (1920); (b) Gilman and Harris, *ibid.*, **49**, 1825 (1927); (c) Gilman, Kirby, Fothergill and Harris, *Proc. Iowa Acad. Sci.*, **34**, 221 (1928); *C. A.*, **22**, 4504 (1928); (d) Gilman and Schulz, THIS JOURNAL, **52**, 3588 (1930); (e) Gilman and Kirby, *ibid.*, **54**, 345 (1932).

[2] (a) Gilman and Crawford, *ibid.*, **45**, 554 (1923); (b) Gilman and Shumaker, *ibid.*, **47**, 514 (1925); (c) Gilman and Peterson, *ibid.*, **48**, 423 (1926); (d) Gilman and McGlumphy, *Rec. trav. chim.*, **47**, 418 (1928).

[3] Wieland and Krause, *Ann.*, **443**, 129 (1925).

[4] Wilson and Hyslop, *J. Chem. Soc.*, **123**, 2612 (1923); **125**, 1556 1924).