WILLIAM F. BRILL¹

Olin-Mathieson Chemical Corp., New Haven, Conn.

Terephthalic Acid by Single-Stage Oxidation

p-Xylene can be oxidized to give high yields of terephthalic acid under mild conditions, using a cobalt catalyst and a ketone activator system

Important variables are oxygen pressure and concentrations of

catalyst
ketone
xylene

TEREPHTHALIC ACID is useful in making condensation polymers, and its preparation by autoxidation of *p*-xylene has received much attention (1, 19). A process has been reported in which yields above 90% were obtained by using a high concentration of cobalt catalyst and a ketone activator (6). This report discusses the effect of reaction variables on the rate and course of this unique reaction.

Experimental

Materials. Cobaltous acetate tetrahydrate was dried at room temperature. Cobaltic acetate was prepared by oxidizing cobaltous acetate in acetic acid in the presence of acetaldehyde (22). Glacial acetic acid contained 0.5% water. Anhydrous acetic acid was prepared with boron triacetate. Liquid reagents were distilled through a 3-foot helices-packed column. p-Xylene was obtained from Oronite Chemical Co. and was designated 98% pure. The major remaining components were m- and o-xylene, ethylbenzene, and toluene. Chloroxylene (boiling point, 183° to 186° C.; n_{D}^{25} , 1.5227) was prepared by the method of Wahl (21). Toluic acid was prepared by oxidizing xylene in the absence of a solvent and recrystallizing twice from benzene. All other materials were purchased and were analytical reagent grade.

Apparatus and General Procedure. When the reaction flask was immersed in a constant temperature bath at 90° C., the temperature measured in the reaction solution itself reached as much as 12° C. higher. Also, it was not possible to operate without an off gas. The first difficulty was overcome by using a Thermocap control relay connected to a 0.2° aniline point thermometer to control a Glas-col mantle which heated only the lower part of the reaction flask. The upper portion of the flask was cooled with air. U.S.P. oxygen passed through a "T" connection to a controlled leak, a potassium hydroxide trap, a water bubbler, a wet test meter, a drying tower, and then into the reaction flask. Exit gas from the reaction left a condenser and passed through a dry-ice trap and traps containing Drierite, or Ascarite and Drierite, and then to a wet test meter.

The reaction solution was pipetted into the reaction flask. After rapid heating to the required temperature, the Thermocap was set, gas flow started, meters zeroed, and magnetic stirring initiated. Off gas was adjusted to between 10 and 12 ml. per minute. When the reaction became exothermic, the cooling air was adjusted.

A standard solution of 1.0M p-xylene, 0.1M cobalt acetate, and 0.1 or 0.2Mmethyl ethyl ketone was prepared for rate studies, which contained 9.2 mg. of water per ml. Analysis (20) showed the three solutions required in the course of the study to be 0.095, 0.094, and 0.096M in cobalt.

Between stirring rates of 800 and 1200 r.p.m., no effect of stirring on the reaction was observed. In this range, a cone of gas extends from the surface of the liquid to the bottom of the flask leaving the Teflon bar exposed. Introducing the gas at the surface gave the same rates as when inlet tubes led below the liquid surface and it avoided plugging with solid product. The effect of oxygen concentration was determined by substituting cyclinders containing

| Produc | cts in N | \oles to | or Sev | eral Re | actions |
|-----------------|-----------------------|----------|--------|---------|---------|
| Ter≠ eph- | <i>p</i> - | Wε | iter | Oxy | gen |
| thalic | Toluic | | Re- | | Re- |
| \mathbf{Acid} | Acid | Found | quired | Found | quired |
| 0.14 | 0.12 | 0.41 | 0.40 | 0.714 | 0.600 |
| 0.15 | 0.11 | 0.44 | 0.46 | 0.746 | 0.615 |
| 0.27 | 0.005 | | | 1.00 | 0.818 |

mixtures of oxygen and nitrogen for the cylinder of pure oxygen usually used. The mixtures were analyzed with a Burrell apparatus and a Beckman oxygen analyzer.

The oxygen consumed during a reaction was determined periodically from the inlet and exit gas wet-test meter readings and was corrected for temperature and the vapor pressure of water.

Water in reaction solutions was determined by the Karl Fischer titration procedure which was checked against prepared standards. Cobaltic ion was titrated by the method of Noyes and Deahl (15). Samples removed directly from the reaction were pipetted into a standard ferrous sulfate solution and back-titrated with permanganate. In the early stages of an oxidation, slightly more permanganate was sometimes consumed than required by the ferrous sulfate blank indicating interference by a reducing agent, perhaps a peroxide. Yields of p-toluic and terephthalic acid in incomplete reactions were determined by diluting with water and partially neutralizing the acetic acid solvent. After filtering the combined solid acids, toluic acid was separated by extraction with alcohol.

| | These Compounds Alkyl Aromatics | May Be Ox | idized Acids |
|------|--------------------------------------|-----------|--|
| | p-Xylene m-Xylene | | Terephthalic Isophthalic |
| FROM | Toluene | то | Benzoic |
| | Chloroxylene o-Xylene p-Toluic | | Chloroterephthalic o-Toluic Terephthalic |

¹ Present address, Petro-Tex Department, Chemical Research and Development Center, Food Machinery and Chemical Corp., Princeton, N. J.

Cobaltic ion reaches 52% of the initial cobaltous acetate concentration in 6.1 hours and then decreases to 44% by 24 hours.

p- and m-Xylene. In a typical reaction, a 1M solution of *p*-xylene in glacial acetic acid, 0.1M in cobalt acetate tetrahydrate, and 0.2M in methyl ethyl ketone is allowed to react with oxygen with efficient stirring at 90° C. and at atmospheric pressure. Following an induction period of approximately 6 hours, characterized by a change in color of the reaction solution from purple to dark green and an increasing rate of oxygen absorption, a rapid reaction ensues, after which the rate gradually decreases. After 24 hours, the reaction was cooled and terephthalic acid filtered out. The product was washed with water or acid until pure white and dried at 100° C. to give a 93% yield. The neutral equivalent was 83 (calculated 83) and ignition residue 0.04%. The dimethyl ester after one recrystallization melted at 140.3° to 140.6° C.

m-Xylene and mixtures of *m*- and *p*-xylene were oxidized in the same manner to give yields of isophthalic acid or mixed dicarboxylic acids of about 93%. The filtrate from all oxidations could be made up to the initial concentrations in xylene and ketone and the reaction duplicated.

Other Alkyl Benzenes. The oxidation of 42 grams (0.3 mole) of chloroxylene in 300 ml. of acetic acid containing 4.2 grams (0.06 mole) of methyl ethyl ketone and 7.5 grams (0.03 mole) of cobalt acetate at 90° C. for 28 hours gave 35 grams of chloroterephthalic acid or 58.5% yield. When this was repeated after adding 2 ml. of methyl ethyl ketone peroxide (Lupersol DDM) to eliminate the induction period, 40 grams of product were obtained in 31 hours. The dimethyl ester (melting point 56° to 58°) was prepared in 82% yield by heating a methanol solution saturated with hydrogen chloride for 4 hours. Dilution of the oxidation filtrate yielded 3-chloro-4-methylbenzoic acid. Recrystallization from 50% methanol gave a melting point of 196° C. [reported 194–6° C. (7)].

One mole of toluene in 500 ml. of acetic acid was oxidized in the usual manner at 90° C. for 24 hours to give an 89% yield of pure benzoic acid.

The oxidation of 34 grams (0.25 mole) of p-toluic acid in 250 ml. of solution containing 1.8 grams (0.025 mole) of methyl ethyl ketone and 6.2 grams (0.025 mole) of cobalt acetate at 90° C. ran 31 hours. Rapid consumption of oxygen began after 10 hours. Filtration of the reaction mixture gave 34.1 grams, (82% yield) of terephthalic acid with a neutral equivalent of 84.

Ethylbenzene was oxidized at 90° C. for 48 hours. The solution was diluted



Halving the methyl ethyl ketone concentration does not affect the maximum xylene oxidation rate

Ketone concentration: A, 0.2M; B, 0.1M

with ice water and made just alkaline with 20% potassium hydroxide and then acid with hydrochloric acid. Extraction with ether and removal of the ether gave 22.5 grams of residue. Fractionation gave 9.2 grams of ethylbenzene at 45° C. (and 30 mm. of mercury), and 9 grams (25% yield) of acetophenone at 102° C. and 30 mm. of mercury, identified by its 2,4-dinitrophenylhydrazone derivative.

A liter of solution containing 106 grams (1.0 mole) of o-xylene, 24.9 grams (0.34 mole) of methyl ethyl ketone, and 24.9 grams (0.1 mole) of cobalt acetate was oxidized for 24 hours at 90° C. Solvent was removed by distillation and the residue added to 100 ml. of hydrochloric acid which was then diluted to 3.0 liters with water. The product was filtered, washed, and dried to give 92.5 grams (68% yield) of o-toluic acid with a melting point of 98° C. and a neutral equivalent of 135 (calculated 136).

Any retarding effect of carboxyl group cannot result from an intermolecular effect. This was demonstrated by the oxidation of 1.0Mtoluene in the presence of 10% benzoic acid. Compared to toluene alone, the induction period was unchanged and, although the second-order plot did not fit well, the rate appeared to be slightly faster.

Other Experiments with p-Xylene. To test the effect of base, a standard oxidation was made, using 0.1M potassium acetate. There was no change in rate or yield. On the other hand, the use of a strong soluble acid, trichloracetic acid, was detrimental—negligible oxygen was consumed in 24 hours. The addition of 2 ml. of either methyl ethyl ketone peroxide or a 25% solution of acetyl peroxide was effective in shortening the induction period to 4.5 and 4.6 hours, respectively, but had no

effect on the rate. Benzoyl peroxide, di-tert-butyl peroxide, or tert-butyl hydroperoxide were unable to shorten the induction period. Ketones, in addition to numerous other compounds unsuitable for the present reaction, were first employed as initiators by Loder who obtained a 2.0% yield of phthalic acids from mixed xylenes (14).

Results and Discussion

Reaction conditions are limited to the use of cobalt and a ketone containing an α -methylene group. Thus, with manganese acetate, nickel acetate, potassium permanganate, and chromium acetate the oxidation fails. 2,5-Hexanedione successfully activates the catalyst but acetone does not. Aldehydes are active but are consumed rapidly and must be used in greater than molar quantities (9, 10). Formaldehyde, trioxane, and paraformaldehyde failed to function.

A sigma rate curve, typical of many autocatalytic reactions, is obtained by following the oxygen consumed with time. This was of little use in assessing the effect of reaction variables on rate. However, in the illustrated plot of $1/C_{\text{methyl}}$ vs. time, curve A gave a straight line whose slope was used for rate comparisons. A specific rate could not be obtained primarily because rate depends on oxygen concentration and concentration of a gas in a solvent is difficult to measure under nonequilibrium conditions. The induction period, taken as the intersection of the line with the time axis, is reproducible within approximately 10%.

With the efficient agitation used, consumption of oxygen was never linear with time; therefore rate is not expected to be diffusion-limited and the treatment described is valid. The reaction does appear independent of rapid stirring speeds, although with very slow agitation, both the rate and yields are strongly affected.

By determining the water and carboxylic acids formed for both the completed and several interrupted reactions, the over-all reaction can be ascertained:

$$CH_{3} \longrightarrow CH_{3} + 3O_{2} \rightarrow HOOC \longrightarrow COOH + 2H_{2}O \quad (1)$$

The oxygen consumed is always higher than that required by the products shown on the right. The oxidations of methyl ethyl ketone and cobaltous ion, although they do not proceed to completion, theoretically require slightly more than 10% as much oxygen as Reaction 1, and along with the formation of carbon dioxide they help to account for the excess oxygen consumed.

That small amounts of added water affect oxidation rate only slightly (Table I) might result from the change in solva-

| | T | ER | ËΡ | H١ | гн | AL | IC | A | CID |
|--|---|----|----|----|----|----|----|---|-----|
|--|---|----|----|----|----|----|----|---|-----|

| Table I. | Water Aff of p-Xy | ects the C /leneª | Dxidation |
|----------------|----------------------|----------------------|-----------|
| Added Water | Total Water | Rolativo | Induction |
| Ml./L. | Ml./L. | Rate | Min. |
| None | 9.2 | 1.00^{b} | 370 |
| 16.5 | 25.7 | 0.94 | 390 |
| 82.2 | 91.7 | 0.80 | c |
| 165.0 | 174.2 | 0.80 | c |
| None | 9.2 | 1.00^{d} | 150 |
| 33.0 | 42.2 | 0.71 | 310 |
| 82.5 | 01 7 | | |

^a 0.92*M p*-xylene, 0.09*M* cobalt acetate. ^b 0.18*M* Methyl ethyl ketone at 90° C. ^c Water added after linear rate obtained. ^d 0.092*M* methyl ethyl ketone at 100° C. ^e No absorption.

tion for the cobalt catalyst. In contrast, the induction period is increased and no reaction with oxygen occurs when 9.2% water is present. The rates given for reactions containing this quantity or more of water are obtained by adding the water after initiation and attainment of a linear rate in the absence of water. A slight secondary induction period is then observed, followed by a linear plot. Although some complication may be introduced by the effect of water on the oxygen solubility, the marked effect of water on the initiation process appears to be real. When water normally present in the glacial acetic acid medium and water of hydration of cobaltous acetate is removed with acetic anhydride, catalyst precipitates from solution and no reaction occurs.

An inverse relationship between rate and temperature, holds between 100° and 70° C. (Table II), the reaction being most rapid at the lower temperature. A very strong and more expected effect is exerted on the induction period which increases from approximately 3 hours at 100° C. to 27 hours at 70° C. Lowering the reaction temperature to 60° C., which required initiation at 100° C., shows the

| Table II. | Effect of Not Pre | f Tempera dictable | ture Was |
|-----------------------------|---------------------------------|----------------------------|--------------------------------------|
| ° C. | Relative Rate ^a | Induction Period | O_2 Solu- bility ^b |
| 100 90 80 70 70 | 1.0 1.8 4.4 4.9 3.9 | 2.5 6.0 12.9 27.1 | 10.4 14.6 17.2 19.7 19.7 |

^a 1.0*M p*-xylene, 0.1*M* cobalt acetate; K = 0.28 l. mole⁻¹ hr.⁻¹ at 90° C. ^b Calculated with the Henry's law constants for water (12) and the vapor pressure data for acetic acid, *p*-xylene, and methyl ethyl ketone (13). ^c 3.5 hr. at 100° C. usually anticipated rate decrease but cannot be considered comparable to a reaction initiated and maintained at a single temperature. This is evident from the slower rate resulting at 70° C., when the induction period is first shortened by initiation at 100° C.

The apparent negative activation energy is probably a reflection of the change in oxygen solubility with temperature. Using equilibrium values and assuming, in the absence of the desired data, the solubility of oxygen in acetic acid to be close to that in water, it can be shown that to obtain a decrease in rate with a rise in temperature, a dependency on oxygen concentration to greater than the second power is required. High dependencies have been reported rarely but were supported in the present case by a study of the effect of oxygen pressure. It is interesting to note that the quantity of oxygen assumed in solution at 80° C, would be entirely consumed in 0.02 minute if removed at the absorption rate observed at 50% reacted.

The effect of oxygen concentration was studied using various mixtures of oxygen and nitrogen under conditions identical to those employed with pure oxygen. The results, shown in Table III, indicate that a decrease in oxygen pressure results in a decrease in rate and increase in inhibition period. The lack of reaction with 20% oxygen is surprising, because it is difficult to visualize an acceptable initiation process so strongly dependent on oxygen concentration.

The concentration of added cobaltous acetate within the range covered has little effect on the rate (Table IV). The induction period, however, has a strong inverse dependence on catalyst concentrations. This sets a lower limit on the quantity of catalyst which may be used; a concentration as low as 0.016M leads to an impractical induction period of 28.4 hours. Even this concentration of catalyst is greater than that usually employed in autoxidations, clearly indicating that high catalyst concentration is one of the unique characteristics of the present reaction.

The role of the catalyst and its relationship to ketone is related to the production of cobaltic ion and the oxidation behavior of methyl ethyl ketone alone. The concentration of cobaltic ion found in final reaction mixtures obtained from oxidations under various conditions show that conditions favoring the rate are accompanied by high conversions of cobaltous to cobaltic ion. Thus, the oxidation at 80° C. left 59% of the catalyst in the higher oxidation state.

Only two concentrations of the methyl ethyl ketone "activator," 0.1M and 0.2M, were studied. At the lower concentration, curve B in the illustration

| Table III. | Dependency Was Strong | on | Oxygen |
|-----------------------|--|-----------|---------------------|
| % Oxygen | $egin{array}{c} { m Relative} \ { m Rate}^{a} \end{array}$ | In Per | duction iod, Hr. |
| 100 90 74 20 | 1.00 0.56 0.13 0.02 | | |

 a 1.0M $\,$ p-xylene, 0.1M cobalt acetate, 0.2M methyl ethyl ketone at 90° C $\,^b$ Started with 100% oxygen.

shows an abrupt decrease in the rate at $^{2}/_{3}$ reacted, both at 90° and 100° C. At the higher concentration this phenomenon is eliminated and the rate is the same as the early rate obtained at the lower concentration. A partial function of the ketone may be to chelate the catalyst, a minimum concentration being required for this purpose. The oxidation of methyl ethyl ketone alone to acetic acid has been extensively investigated (18) but not under conditions resembling those occurring in the present case. Therefore, an oxidation of 0.2Mmethyl ethyl ketone in the absence of p-xylene was conducted using a 0.09Msolution of cobalt acetate in glacial acetic acid at 100° C. The data fit a first-order plot and give a k_1 value of 1.37×10^{-2} min.⁻¹ The half life of 50 minutes for methyl ethyl ketone alone is considerably less than the 714-minute half life of the *p*-xylene oxidation at this temperature.

The net result of oxidizing methyl ethyl ketone alone in the presence of a high cobalt concentration is to produce an active catalytic solution, for when 0.5 mole of p-xylene is added to the final oxidate obtained, the oxidation proceeds readily until 71% of theoretical oxygen is consumed. It appears that cobaltic ion functions as an initiator and that an

Table IV. Effect of p-Xylene and Catalyst Concentrations

| - •• | $p	ext{-}Xylene$ | |
|--|---|----------------------------|
| Mole/L. | $egin{array}{c} { m Relative} \\ { m Rate} \end{array}$ | Induction Period, Hr. |
| 1.0^{a} 0.75 a 0.50 a 0.50 b | 1.0 1.8 3.2 3.8 | 6.2 7.15 7.6 13.2 |
| | Cobalt Acetate ^c | |
| 0.100 0.050 0.016 | 1.0 1.2 1.0 | 6.2 14.4 28.4 |

 a 0.1*M* cobalt acetate, 0.2*M* methyl ethlyl ketone. b 0.05*M* cobalt acetate, 0.1*M* methyl ethyl ketone. c 1.0*M p*-xylene, 0.2*M* methyl ethyl ketone.

oxidizing mixture of p-xylene alone is not effective in maintaining the required cobaltic concentration. A more quantitative check is obtained by oxidizing *p*-xylene in the absence of any ketone with a 0.2M concentration of separately prepared cobaltic acetate. After an induction period of 6 hours, a relative rate the same as that usually obtained with cobaltous acetate and ketone is obtained. At 60% reacted, the relative rate then falls to 0.36. Despite the ease of oxidation of methyl ethyl ketone some of it is able to survive the oxidation of the p-xylene because at 87% reacted, a quantity of ketone equivalent to 4% of its initial concentration was isolated as its 2,4 - dinitrophenylhydrazone. This, along with the falling off of the rate at the lower ketone concentrations as with cobaltic acetate alone, is consistent with a role for the ketone of not only producing cobaltic ion during the induction period but of maintaining the required ratio of cobaltic to cobaltous ion after the maximum rate is attained.

Using the usual 0.2M methyl ethyl ketone and 0.1M cobalt acetate, decreasing initial p-xylene concentration results in an increase in rate (Table IV). That this inverse relationship is not caused by the increase in the activator and catalyst to p-xylene ratio is shown using concentrations of ketone and cobalt of 0.1M and 0.05M, respectively. Decreasing the initial *p*-xylene concentration effects only a slight increase in the induction period.

The Oxidation of Other Alkyl Benzenes. Several other alkyl aromatic compounds (Table V) were investigated with somewhat surprising results. No very large differences in rates are observed for any of the disubstituted benzenes. The behavior of *p*-toluic acid, as anticipated, and of pxylene does not conform to the concept that a *p*-carboxyl substituent strongly inactivates the oxidation of a methyl group (1). This effect is only retarding and a 92% yield of terephthalic acid was actually obtained from *p*-toluic acid. However, when the carboxyl group is in

the ortho position the methyl group becomes strongly resistant to oxidation as o-xylene yields only o-toluic acid. When the rate for *o*-xylene is calculated on the basis of a single methyl being available for oxidation, it is found to be only 0.37times that of toluene; this indicates that even o-methyl has a retarding effect. The effect is further demonstrated by chloroxylene whose rate is not only less than that of *p*-xylene but which yields 3-chloro-4-methylbenzoic acid and no 2-chloro-4-methylbenzoic acid as the by-product. incompletely oxidized Chloroxylene may be forced by long reaction times to yield the terephthalic acid derivative.

A crude analysis of the effect of meta and para substitution indicates that the rate decreases in going from methyl to chlorine to carboxyl. The effect of a single meta or para methyl group $(R_x$ in Table V) may be obtained by considering the rates for the xylenes to be an average of the effects of carboxyl and methyl. On applying these values to the Hammett equation (8), a good straight line relationship is observed yielding a rho value of -0.95. This indicates oxidation is favored by a high electron density at the reaction site. Although it is logical to assume that highly positive cobalt is involved in a step slow enough to influence the rate, it must be pointed out that polar effects have frequently been observed for the attack of neutral free radicals on benzylic hydrogen (11). For the noncatalytic oxidation of aralkyl hydrocarbons, Russell (16) has reported a negative rho for the propagation steps.

Mechanism. High catalyst concentration requirements and gradual transformation of the catalyst to the higher valency state in the period preceding the maximum oxidation rate suggest the following initiation step:

 $Co^{+++} + RH \rightarrow Co^{++}R + H^+$

This reaction was advanced (3) for the oxidation of trimethylethylene in acetic acid.

The cobaltic ion is regenerated by the reoxidation of cobaltous ion by hydro-

Table V. Other Alkyl Aromatic Compounds May Also Be Oxidized

| Compound ^a | Relative Rate, <i>R</i> | Induction Period, Hr. | $Product, ^{b}$ Acid | ${f Best^b}\ {f Yield},\ \%$ | X° | $R_x{}^d$ |
|---------------------------|----------------------------|-----------------------------|-------------------------|------------------------------|----------------------------|-----------|
| <i>p</i> - X vlene | 1.00 | 6 | Terephthalic | 95 | $p-CH_3$ | 1.75 |
| m-Xylene | 0.69 | 7 | Isophthalic | 90 | m-CH ₃ | 1.13° |
| Toluene | 1.00 | 11 | Benzoic | 89 | н | 1.0 |
| Chloroxylene | 0.65^{d} | 6 | Chiorotere- phthalic | 75 | m-Cl, p-CH ₃ | 0.65 |
| o-Xylene | 0.22 | 4 | o-Toluic | 76 | $o-CH_3$ | 0.37 |
| <i>p</i> -Toluic | 0.25 | 10 | Terephthalic | 92 | p-COOH | 0.25 |
| Ethylbenzene | Slow | None | (Acetophenone) | 25 | | |

^a 1.0*M*. ^b Reaction times extended until no further reaction occurs—usually 24 hr. or more. ^d Relative rate calculated for oxidation of single methyl group. $e_{R_x} = 2R$ ---° In XArCH3. R_{COOH} .

peroxide formed in the now commonly accepted propagation steps (5) which involve a reaction of the alkyl radical with oxygen to produce a peroxy radical, followed by hydrogen abstraction. In the present case, the increased stability of benzyl radicals should lead to shorter chains while benzyl hydroperoxides may not efficiently regenerate cobaltic ion and radical fragments capable of initiation. The function of the more easily oxidized ketone may then be to produce a peroxide capable of readily oxidizing cobaltous ion. Peroxy radicals produced in the ketone oxidation may also be capable of chain transfer by hydrogen abstraction with the hydrocarbon but, because ketone concentration does not have a direct effect on rate, this does not seem to be a dominant factor. The complicated nature of cobalt acetate in acetic acid is well recognized (4, 17) and complexing with the ketone is also involved. Oxidation of the aldehyde produced on hydroperoxide decomposition. is a rapid reaction proceeding through the peracid and yielding the final carboxylic acid product (2).

Literature Cited

- (1) Astle, M. J., "Chemistry of Petro-chemicals," p. 174, Reinhold, New York, 1956.
- (2) Bawn, C. E. H., Jolly, J. E., Proc. Roy. Soc. (London) A237, 297 (1956).
 (3) Bawn, C. E. H., Pennington, A. A., Tipper, C. F. H., Discussions Faraday Soc. 10, 290 (1951).
 (4) Bawm, C. E. H. St. T. J. C.

- Soc. 10, 290 (1951).
 (4) Bawn, C. E. H., Sharp, J., J. Chem. Soc. 1957, p. 1866.
 (5) Bolland, J. L., Quart. Rev. (London) 3, 1 (1949).
 (6) Brill, W. F. (to Olin Mathieson Chem. Corp.) U. S. Patent 2,853,514 (Sept. 23, 1056) 1958).
- (7) Gerichten, E. V., Ber. 11, 365 (1878).
 (8) Hammett, L. P., "Physical Organic Chemistry," p. 186, McGraw-Hill, New York, 1940.
- (9) Hull, D. C. (to Eastman Kodak Co.),
 U. S. Patent 2,287,803 (June 30, 1943).
 (10) *Ibid.*, 2,673,217 (March 23, 1954).
 (11) Huyser, E. S., J. Am. Chem. Soc. 82,
- 394 (1960).
- (12) International Critical Tables, Vol. III, p. 257, McGraw-Hill, New York, 1928.
- (13) Jordan, T. E., "Vapor Pressure of Organic Compounds," Interscience, New York, 1954.
- (14) Loder, D. J. (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,245,528 (June 10, 1941).

- (June 10, 1941).
 (15) Noyes, A. A., Deahl, T. J., J. Am. Chem. Soc. 59, 1337 (1937).
 (16) Russell, G. A., Ibid., 78, 1047 (1956).
 (17) Sharp, J., J. Chem. Soc. 1957, p. 2030.
 (18) Shell Chemical Corp., "Methyl Ethyl Ketone," Tech. Publ. SC, 50-2, p. 92, New York, N. Y., 1952.
 (19) Toland, W. G., IND. ENG. CHEM. 50, 1386 (1958).
 (20) Tomech, O., Freiberger, F., J. Am. Chem. Soc. 57, 801 (1935).
 (21) Wahl, H., Compt. rend. 196, 1900-2 (1933).

- (1933).
- (22) Walker, W. O. (to A. O. Smith Corp.), U. S. Patent 1,976,757 (Oct. 16, 1934).

RECEIVED for review September 21, 1959 ACCEPTED July 5, 1960