52. *Autoxidation Processes. Part IX. The Electrolytic Dissociation of α-Ketols.*

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The rates of autoxidation, oxidation with Fehling solution, and racemisation of α-ketols are proportional to the concentrations of alkali in the reacting solutions (Weissberger *et al.*, *Ber.*, 1929, **62**, 1942; 1931, **64**, 1200; *Annalen*, 1930, **478**, 112; **481**, 68; 1933, **502**, 53); this led to the conclusion than an electrolytic dissociation of the ketol is the first step in these processes. Furthermore, a relation has been established (see Part VIII, preceding paper) between the rates of these reactions of the ketols and the dissociation constants of the corresponding carboxylic acids. This seems to indicate that the ability both of the ketol group and of the carboxylic group to undergo electrolytic dissociation is similarly influenced by the radicals attached to them. Exceptions to this relation are found in certain *o*-substituted ketols where steric hindrance comes into play (see Part VIII).

For the further investigation of these phenomena, it seemed desirable to obtain more detailed knowledge about the dissociation of the α-ketols. The method developed for this purpose promises to be useful also for other problems dealing with substances which are insoluble or but sparingly soluble in water.

The small solubility in water of most of the ketols in question prevented measurements in aqueous solution, but ethyl alcohol was a suitable solvent. This excluded potentiometric measurements, as being not sufficiently exact, and also direct determination of the conductivity because this was too small. We therefore measured the decreases in conductivity which a 0·01*N*-solution of sodium hydroxide in 90% ethyl alcohol undergoes on the addition of the ketols to a concentration of 0·02*M*.

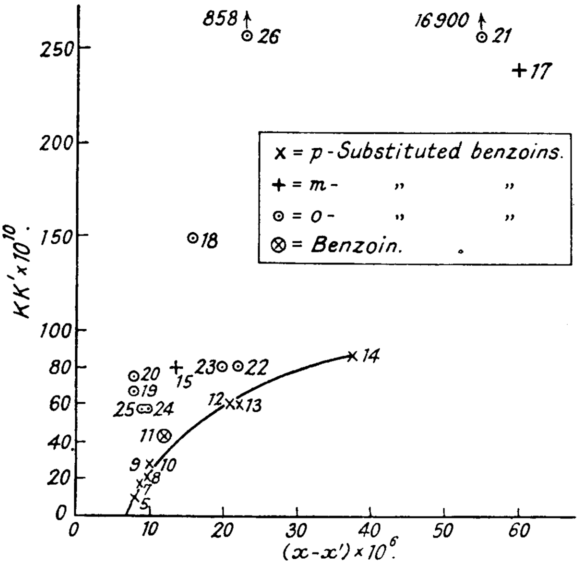
The significance of these values appears from the following considerations. The conductivity of the aqueous-alcoholic solutions of sodium hydroxide is equal to the sum of the products of the concentration and migration velocity of the ions $Na^{\cdot}$, HO', and C_2H_5O'. For our solutions, we may further assume that the dissociation of the hydroxide, of the ethoxide in equilibrium with it, and of the sodium salts of the α-ketols is practically complete. Therefore, on the addition of the ketol, the concentrations of sodium ions and of the anions will remain constant. A certain amount of the hydroxide and ethoxide ions, however, will be replaced by the anions of the ketol. The migration velocities of these are considerably smaller than those of the hydroxide and ethoxide ions, but for the different ketols under investigation they may be assumed to be practically the same. The decreases in conductivity, therefore, are the consequence of the replacement of the hydroxide and ethoxide ions by the ketol ions, and are proportional to the concentrations of the latter. Since the total concentration of the ketol in our experiments is high (0·02*M*), and the fraction dissociated very small, the denominator in the law of mass action which defines the dissociation constants can be taken as constant in our solutions, and therefore the measured decrease is proportional to the dissociation constant. The measurements have been extended to some other comparison substances (p. 228), which may be of use for other purposes.

Experimental.

Measurements.—Conductivities were determined by Kohlrausch's method with induction coil and telephone. The resistance of the Wheatstone bridge (1000 mm. long) was 17·62 ohms: it was extended by a resistance of 200 ohms, so its length was equivalent to 12,290 mm. The minima were well defined within 1 mm. It proved best to use a cell of high constant (1·02); this was made of glass, with electrodes consisting of very thin platinised platinum pins, 1·2 mm. thick and 10 mm. long, about 10 mm. apart. The temperature of the thermostat was 20·0° ± 0·02°. The solvent alcohol was purified from aldehyde according to Danner and Hildebrand (*J. Amer. Chem. Soc.*, 1922, **44**, 2824). The alcoholic sodium hydroxide solution was freshly prepared for each measurement by diluting 20 c.c. of carbonate-free 0·1*N*-sodium hydroxide (Fixanal) with alcohol to 100 c.c. For the measurement, 25 c.c. of this 0·02*N*-sodium hydroxide solution were mixed with 25 c.c. of either alcohol or a 0·04*M*-alcoholic solution of the ketol. The solutions had been previously freed from oxygen by a stream of nitrogen, which was purified by alkaline pyrogallol solution and red-hot copper and saturated with the vapour of the solvent. For this purpose and for the mixing, we used a round-bottomed flask fitted with a dropping funnel and with tubes for the introduction and the escape of the gas and for transferring the liquid into the conductivity cell. One of the solutions was placed in the flask, the other in the funnel, nitrogen passed through for 20 minutes, then the solutions were mixed by opening the tap of the funnel, stirred by the gas stream, and transferred through the communicating tube to the cell, which was filled with nitrogen. All exit tubes for the gas had liquid seals.

Before each measurement, the apparatus was tested by a measurement of a 0·01*N*-sodium hydroxide solution; the deviations in these measurements, as well as those of the solutions containing the ketols, which were measured several times, never exceeded 1·5 mm. on the bridge. The differences between the conductivities of the pure sodium hydroxide solutions and the solutions containing the ketols were 17—130 mm. The first measurement was carried out 10 minutes after the mixing. A change in the conductivity after 1 hr.'s standing in the cell was observed only with the chlorobenzoins, but even there it did not exceed 2 mm. on the bridge. The values given in the last cols. of Tables I—III of the preceding paper are the differences between the conductivity of the 0·01*N*-sodium hydroxide solution (x) and that of the solutions containing 0·01*N*-sodium hydroxide and 0·02*M*-α-ketol (x'). Each value of $x - x'$ is the average of more than one independent measurement.

FIG. 1.



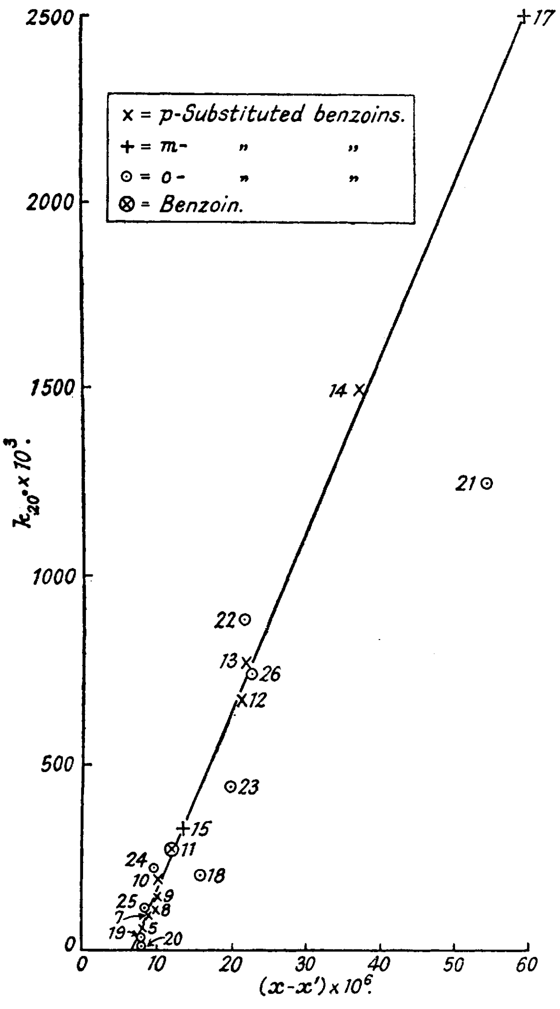
DISCUSSION.

It must first be emphasised that the benzoins with a *different substituent* in each ring isomerise in alkaline solution to an equilibrium. The rate of this isomerisation can be assumed to be identical with the racemisation velocities of the respective optically active benzoins, because it is highly probable that the intermediate product of both processes is identical. In any case, the isomerisation will not be the faster process. Since the racemisation velocities in the cases hitherto investigated (Weissberger *et al.*, *loc. cit.*) are identical with those of the autoxidation, the latter provide the data for the calculation of the amounts to which the benzoins in question will have isomerised before the actual measurements. An uncertainty is introduced into these calculations, however, by the possible influence of the solvent. The autoxidation rates are determined in 79% ethyl alcohol, and the conductivities in 90% alcohol; now the velocity of autoxidation is approximately doubled by a change of solvent from 45% to 79% alcohol (*loc. cit.*), but measurements with benzoin showed that the further increase caused by changing to 90% alcohol is only about 20%. Therefore, the extent of isomerisation before the measurement takes place is less than 5% with the *p*-methyl- and the *o*-ethoxy-benzoins, and less than 20% with the other unsymmetrical benzoins. The smallness of the differences between the values of $x - x'$ for the isomeric benzoins in question, therefore, is genuine and not due to previous isomerisation. This is in agreement with the differences in the autoxidation rates of the "unsymmetrical" benzoins: since the intermediate for the isomerisation reacts completely with the oxygen if the latter is abundant (*Ber.*, **1931**, **64**, 1200), no isomerisation can interfere with the autoxidation measurements.

To illustrate the relation between the electrolytic dissociation of the ketols and of the corresponding carboxylic acids, the values of $x - x'$ are plotted against the products of the dissociation constants of the latter in Fig. 1. The points for the *p*-substituted compounds are situated *on one curve* : a variation which alters the dissociation constants of the acids gives rise to a corresponding change in the dissociation of the ketols. The similarity of the groups –CO·OH and $-CO\cdot\dot{\underset{\cdot}{C}}\cdot OH$ is close enough to provide for this kinship, even though the absolute values of the dissociation constants of the carboxylic acids are about six orders of magnitude higher than those of the ketols.

The estimation of the absolute values of the dissociation constants of the ketols is possible from the $x - x'$ values of the substances given below, the electrolytic dissociation constants of which are recorded in the literature. The value of benzophenone-oxime, the molecular size of which is similar to that of the benzoins, shows that when $10^6(x - x') = 50$, the dissociation constant is of the order of 10^{-12}. As to the other two substances, one must bear in mind that their smaller molecular sizes — higher migration velocities—diminish the effect in $x - x'$.

FIG. 2.



	$(x - x')\ 10^6$.	K.
Glycol	2·3	6×10^{-15}
Acetoneoxime	20·4	6×10^{-13}
Benzophenoneoxime	55·1	5×10^{-12}

Of the *m*-derivatives, only two have been measured, but a similar curve plotted through them would lie above that for the *p*-substituted substances : introduction of substituents into the *m*-position seems to raise the dissociation of the acids more than that of the ketols. The value for benzoin itself falls between the two curves.

These results are in full agreement with the observation that the ratio of k to K (see p. 224) is smaller with *m*- than with *p*-substituted compounds.

The *o*-substituted compounds give widely scattered points, and the displacement from the curve for the *p*-derivatives is the greater the smaller the ratios in col. 5 (Table III, p. 224), *i.e.*, the greater the effect there characterised as steric hindrance. If, however, we plot $x - x'$ against the *autoxidation rates* (Fig. 2) * a close proportionality is seen to hold between the two properties for all the compounds, including the *o*-derivatives : the small deviations with *oo'*-diethoxy- and *oo'*-dimethoxy-benzoin are within the limits of experimental error. It should be remembered that for *oo'*-diethoxybenzoin the close coincidence of autoxidation rate and racemisation velocity (*loc. cit.*) showed that the steric hindrance cannot be attributed to any phase in the autoxidation process which is subsequent to that in which the racemisation occurs. Those deviations, therefore, are without significance for the essential steric hindrance. Even with *oo'*-dimethyl- and *oo'*-dichloro-benzoin, however, the deviations are small in comparison with the amounts under discussion.

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* The rate of autoxidation of *mm'*-dichlorobenzene was too high for direct measurement at 20°, and was calculated from that at 10° with the average temperature coefficient.

It follows that the steric hindrance in autoxidation, oxidation with Fehling solution, and racemisation of the α-ketols takes place in their *electrolytic dissociation*. This may be considered as evidence for the theory of dissociation of acids according to which the process involves the *approach of a molecule or ion, e.g.*, $AcOH + H_2O \rightleftharpoons (AcOH_3O) \rightleftharpoons AcO' + H_3O^{\cdot}$. It should be pointed out that, as has been shown in Part VIII, not only the size but also the charge of the *o*-substituents is of importance in steric hindrance: chlorine with its negative field has an exceptionally strong effect. This suggests that the dissociation at least of very *weak acids*, like that of the ketols, involves the approach of a *negative* particle which may be hindered, not only by the volume of a substituent, but also by the electrostatic repulsion of a negative substituent according to the mechanism $AcOH + HO' \rightleftharpoons AcO' + H_2O$.

The observation that *o*-substitution in the ring adjacent to the hydroxyl group is more effective in its hindrance than the same substitution in the other ring, obviously agrees with the interpretation given above.

In subsequent papers there will be discussed the mechanism of the autoxidation and the related processes, and the reason for the failure of the curve in Fig. 2 to pass through the origin.

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[*Received, January* **2nd, 1935.**]