Interconversions of Itaconic and Citraconic Anhydride in Amine Solutions.

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The isomerization of itaconic to citraconic anhydride in dimethylaniline solution has been shown spectrophotometrically to be a first-order reaction; the activation energy is about 15 kcal./mole and the temperature-independent factor about $2{\cdot}5 \times 10^9$ min.$^{-1}$. Other complex-forming aromatic solvents, *e.g.*, anisole or mesitylene, do not catalyse the conversion to a significant extent.

Aliphatic tertiary amines and itaconic anhydride instantaneously form a deep-magenta-coloured complex which then slowly changes to an unidentified reddish-brown product; the same product is also formed slowly from citraconic anhydride in aliphatic amine solution. Ammonia and primary and secondary amines also instantaneously form magenta complexes with itaconic anhydride, but these fade extremely rapidly owing to amide formation. A solution of itaconic anhydride is suggested as an easy specific reagent for tertiary aliphatic amines.

During investigations on coloured molecular complexes of maleic anhydride and its derivatives Pfeiffer and Böttler (*Ber.*, 1918, **51**, 1819) observed that dimethylaniline catalysed the isomerization of itaconic anhydride to citraconic anhydride. Citraconic anhydride dissolved in dimethylaniline instantaneously gives an orange colour, ascribable to a molecular complex. Itaconic anhydride gives a solution which is initially pale yellow but slowly assumes the same colour as the citraconic anhydride solution; when such a solution is treated with alkali and then acidified, citraconic acid is obtained. In the absence of a solvent the conversion of itaconic into citraconic anhydride only takes place at high temperatures (cf. *Org. Synth.*, Coll. Vol. II, John Wiley & Sons, Inc., New York, 1943; also p. 1650).

Two causes of the catalytic effect of dimethylaniline suggest themselves: the reaction may simply be base-catalysed; or the ease of isomerization in dimethylaniline may be linked in some way with the formation of a complex between the solvent and the product. At its simplest, the latter may be regarded as a lowering of the energy level of the transition state accompanying the lowering of the energy level of the final state. (A simple inorganic example is the increased rate of autoxidation of ferrous ions in the presence of substances which form complexes with ferric ion.) Since, according to Pfeiffer and Böttler (*loc. cit.*), durene, methyl *o*-tolyl ether, and quinol (all of which form complexes with citraconic anhydride) do not cause the isomerization of itaconic anhydride, it seemed *a priori* more probable that the isomerization in dimethylaniline is due to the basic nature of the solvent.

Spectrophotometric Measurements in Dimethylaniline Solution

Materials.—Dimethylaniline was freed from primary and secondary amines by refluxing with acetic anhydride, and was then fractionally distilled through a 12" column containing Fenske helices. Citraconic anhydride was a commercial sample, fractionally redistilled under reduced pressure (b. p. 71°/7 mm.). Itaconic anhydride was prepared from commercial itaconic acid and thionyl chloride (Meyer, *Monatsh.*, 1901, **22**, 422) and was twice recrystallized (m. p. 65—66°) from chloroform–ether.

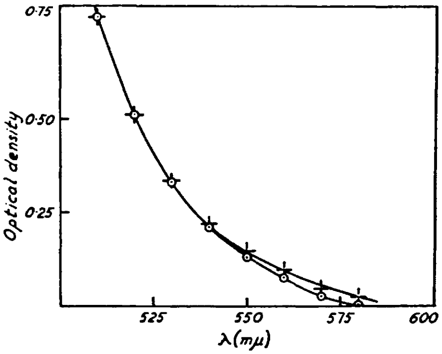
Technique of Measurement.—Optical density was measured (*a*) on a Unicam Quartz Spectrophotometer Model S.P. 500, using 1 cm. or 2 mm. cells, and (*b*) on a Hilger " Spekker " absorptiometer, using a mercury lamp source, Ilford Filter 603 to isolate the 4916 Å line or a combination of Ilford Filter 605 and Chance Filter OB2 to isolate the 5461 Å line, and 2·5 mm. or 5 mm. cells. Experiments with the Unicam instrument were carried out at room temperature but measurements on the Spekker absorptiometer were made with the cells carried in a small thermostat bath mounted on the slide. The cell containing the blank and an empty cell were kept in the thermostat for some minutes, the solution of itaconic anhydride then made up as rapidly as possible (finely powdered, it dissolves in dimethylaniline in a matter of seconds), and poured into the cell, this point being taken as zero time.

All measurements were carried out against blanks of dimethylaniline. Calibration curves were constructed; with the Unicam instrument, the D-[citraconic anhydride] plot is linear, where D is the optical density. With the Spekker arrangement, the plots were slightly curved, to an extent indicating about 98% monochromatization. The optical density of itaconic anhydride solutions, extrapolated to zero time, was always negligible (less than 0·01).

The optical density of citraconic anhydride solutions in dimethylaniline decreases by about 7% from 20° to 50°, and this was taken into account in using the calibration curves. No deduction regarding the heat of formation of the absorbing citraconic anhydride–dimethylaniline complex can be made from this, since it is not known whether the equilibrium constant is large or small; if large, it is clear that little change of optical density with temperature would be expected in any case since the fraction of citraconic anhydride present as a complex would remain near unity.

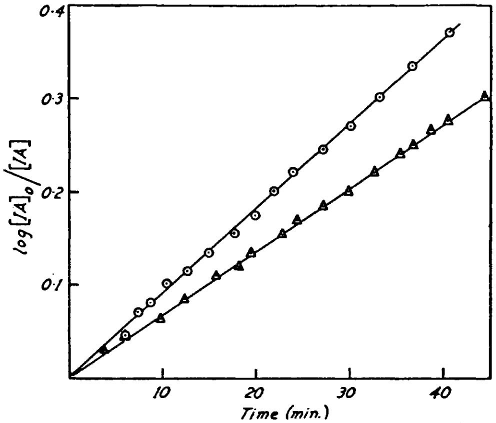
Quantitative Nature of the Conversion, and Kinetic Results.—It is relatively easy to obtain experimental conditions where the optical density of an itaconic anhydride solution after prolonged storage (say overnight) is within ±10% of that for a citraconic anhydride solution. An improvement is difficult as there are two vitiating factors : In dilute solutions of the anhydrides (say <0·5%) traces of water can produce appreciable fading due to hydrolysis. In more concentrated solutions the fading is negligible, but itaconic anhydride induces the autoxidation of dimethylaniline to produce an impurity which absorbs in the yellow region of the spectrum; in such solutions the optical density of citraconic anhydride and "old" itaconic anhydride solutions agree perfectly at shorter wavelengths, but at long wavelengths, the old itaconic anhydride solution has a greater density (cf. Fig. 1). This autoxidation could be roughly halved by the addition of small quantities of quinol to the dimethylaniline. Such solutions gave final optical densities in reasonable agreement with the expected value (within about 5%) even at long wavelengths, if measured against a solution of quinol and dimethylaniline of the same age. Most of the kinetic measurements were carried out in this way (Table). Since the available wavelengths (5461 and 4916 Å) and cells largely determined the concentration of itaconic anhydride which could be used in the kinetic experiments, it was impossible to avoid both the fading and the autoxidation difficulties simultaneously. For λ 5461 Å, fairly concentrated solutions had to be used (of the order 30 g./l.) and the final optical density was (in the absence of quinol) up to 15% higher than the value to be expected if only citraconic anhydride had been produced; for λ 4916 Å, on

FIG. 1. *Optical density of citraconic and itaconic anhydride solutions in dimethylaniline.*



1 cm. cells; c, 10 g./l. ○ = Citraconic anhydride; + = itaconic anhydride after overnight standing.

FIG. 2. *Typical first-order plots.*



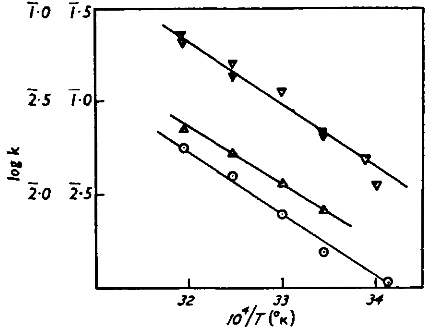
○, Measured at 26° on Spekker, using $\lambda = 5641$ Å. △, measured at 22° on Unicam, using $\lambda = 5400$ Å. Both solutions contained 0·5 g./l. of quinol. $[IA]_0 = 30$ g./l.

First-order velocity constant k for conversion of itaconic anhydride in dimethylaniline solution.

Temp.	Instrument	λ (Å)	$[IA]_0$ (g./l.)	[Quinol] (g./l.)	10^2k (min.$^{-1}$)
21° ± 1°	Unicam	5300	25·0	—	1·24
„	„	5300	5·0	—	1·13
„	„	5400	30·3	0·5	1·22
„	„	5400	30·3	1·0	1·25
22 ± 1	„	5400	30·4	0·5	1·56
26	Spekker	4916	5·0	—	1·56
30	„	„	5·0	—	2·53
35	„	„	5·5	—	4·02
40	„	„	5·1	—	5·68
26°	Spekker	5461	30·5	—	2·67
30	„	„	30·3	—	3·68
35	„	„	29·7	—	5·28
40	„	„	30·0	—	7·15
26	„	„	29·9	0·5	2·07
„	„	„	30·5	„	2·13
30	„	„	29·6	„	3·63
35	„	„	29·9	„	4·30
„	„	„	30·2	„	5·12
40	„	„	29·8	„	6·43
„	„	„	30·9	„	7·12

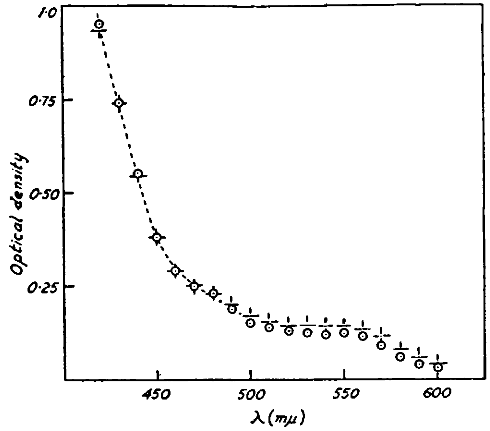
the other hand, the density was up to 15% too low. These errors are of course most significant near the end of the reaction, since the concentration of itaconic anhydride [IA] is calculated as the difference between the initial concentration $[IA]_0$ and the (apparent) amount of citraconic anhydride formed. Consequently, kinetic runs were usually only evaluated to about 60% conversion; some typical results are shown in Fig. 2, which demonstrates that log $[IA]_0/[IA]$ is linear with time, *i.e.*, that the reaction is of first order in [IA]. This first order is also demonstrated by the agreement between values of *k* obtained from experiments at widely different values of $[IA]_0$ (cf. Table).

Fig. 3. *Temperature-dependence of first-order velocity constant k.*



Inner scale for ○ and △, outer scale for ▽.
○ measured at λ = 4916 Å, $[IA]_0$ ~5 g./l.
△ measured at λ = 5461 Å, $[IA]_0$ ~30 g./l.
▽, as △, but 0·5 g./l. of quinol added.

Fig. 4. *Optical density of itaconic* (+) *and citraconic* (○) *anhydride in acetone containing 0·5% of triethylamine, after standing at room temperature for 48 hr.*



Concentration of anhydrides = 5·0 g./l.; 1 cm. cells.

The various values of *k* obtained are given in the Table. It is seen that the measured values for λ 5461 and 4916 Å differ by about 30%, in the sense to be expected from the sources of error just discussed.

The effect of temperature on *k* is shown in Fig. 3. Though the values of *k* fall into three groups, for the reasons discussed, the values of the activation energy agree well, being 14·5, 15·4, and 15·6 kcal./mole respectively; from a mean value of 15·2 kcal./mole, the temperature-independent factor is found to be 2·5 × 10^9 min.$^{-1}$.

Attempts were made to examine the effect of dimethylaniline concentration on the reaction rate, using various diluents. These all failed; the autoxidation of dimethylaniline in the presence of itaconic anhydride was much more pronounced when diluents were used, and could not be adequately suppressed.

Effect of Other Complex-forming Aromatic Solvents.—The stability of itaconic anhydride in benzene, mesitylene, and anisole, which are known to form complexes with maleic anhydride and therefore presumably also with citraconic anhydride (Barb, *Trans. Faraday Soc.*, **1953**, **49**, 143), was examined. In all cases the ultraviolet absorption of citraconic anhydride solutions is much more pronounced than that of itaconic anhydride solutions, so that any conversion was easily detectable.

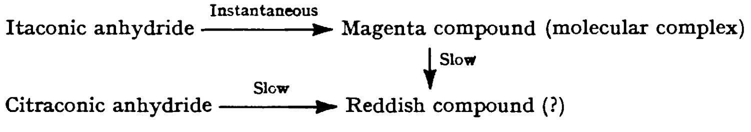
Solutions of itaconic anhydride in benzene were refluxed for up to 11 days; the increase in optical density, if attributed to formation of citraconic anhydride, corresponded to less than 4% conversion. Solutions of itaconic anhydride in mesitylene showed no evidence of isomerization after 24 hr. at 60°. At higher temperatures (130° and 160°) experiments had to be carried out in sealed tubes *in vacuo*, to prevent oxidative side-reactions leading to strongly absorbing products. Under these conditions the isomerization undoubtedly occurs in mesitylene but is still quite slow, *e.g.*, at 160° about 10% was converted in 5 hr. and about 70% in 100 hr. Solutions in anisole behaved similarly, *e.g.*, during 24 hr. about 20% was converted at 130° and about 60% at 160°. In each case it was found that a small quantity of by-product was formed, since the solutions of itaconic anhydride which had been heated showed a slight but definite absorption at wavelengths longer than those at which solutions of citraconic anhydride absorb; at shorter wavelengths the shape of the optical density–wavelength curve was identical with that for citraconic anhydride solution, showing that this was the main product. It was observed that the yield obtained tended to be unduly low in very dilute solutions; this was attributed to hydrolysis by traces of water.

To compare these results with the behaviour of pure itaconic anhydride on heating, a sample of the solid was melted and allowed to resolidify in a tube which was then thoroughly degassed; it was remelted *in vacuo* and again resolidified, and the tube was re-evacuated, sealed off, and heated at 130° for 20 hr. The product was dissolved in anisole and the solution compared with one of citraconic anhydride of similar concentration; the absorption curves were practically coincident, and the conversion was therefore almost complete.

It is concluded that the conversion in other aromatic solvents is very much slower than in dimethylaniline, and only of a similar speed to, or even slower than, the reaction in a melt of pure itaconic anhydride. The catalytic effect of dimethylaniline is therefore not shared by all other solvents which form complexes with citraconic anhydride.

Effect of Aliphatic Tertiary Amines on Itaconic and Citraconic Anhydride Solutions.—On addition of triethylamine (purified by refluxing with acetic anhydride, followed by careful fractional distillation) to a solution of itaconic anhydride in, say, chloroform an extremely intense magenta colour is produced. In a few hours at room temperature the solution changes to a more stable colour varying from purple to reddish-brown. (The final colour appears to depend on the concentrations used and on the diluent; thus solutions in acetone give a more orange colour than those in chloroform.)

In contrast, citraconic anhydride solutions on addition of triethylamine initially give only a pale yellow colour, but in a few hours this intensifies to the reddish colour obtained from the itaconic anhydride solutions. The identical absorption of the final solutions, after 48 hours, is shown in Fig. 4. The reactions with triethylamine are thus :



The magenta-coloured compound is regarded as a loose molecular complex in view of its instantaneous formation when the reagents are mixed, even at low temperatures. Thus, *e.g.*, a 1% solution of itaconic anhydride in chloroform was degassed *in vacuo* and kept frozen in liquid air, and a quarter of its volume of triethylamine was distilled in; when this mixture was allowed to thaw in carbon dioxide–acetone at —60° the magenta colour was formed immediately. At —60° the complex appeared completely stable; at 0° the magenta colour became more brown during several hours.

The nature of the final, stable compound obtainable from the anhydrides was not established. Reaction with pure liquid citraconic anhydride and triethylamine is violent and gives a brittle purplish-black solid which dissolves not only in chloroform but also in water to give a clear intensely coloured solution. In water, this colour fades completely after a few hours.

A variety of compounds structurally related to the anhydrides (itaconic acid, butyl acrylate, maleic anhydride, benzoquinone) were added to triethylamine in chloroform. In each case only a slight yellow colour or no effect at all was produced. As regards different bases, tertiary aliphatic amines as diverse as triethylamine, *N*-ethylethyleneimine, and 1 : 4-di-*n*-butylpiperazine all give similar intense colours with itaconic anhydride. Primary and secondary amines, and even ammonia, give momentary magenta reactions, but the colours in these cases fade extremely rapidly, presumably owing to amide formation. It appears therefore that the formation of the magenta-coloured complexes is highly specific to itaconic anhydride, but shared by all aliphatic amines. The subsequent formation of a more stable coloured compound is only shown by tertiary amines because amide formation cannot supervene. A solution of itaconic anhydride in chloroform is suggested as a sensitive specific reagent, easy to use, for detection of tertiary aliphatic amines.

It is concluded that the catalysis by dimethylaniline of the isomerization of itaconic to citraconic anhydride is a highly specific effect. It is not shown by other aromatic solvents or by aliphatic tertiary amines.

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