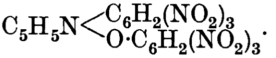
CCCXXI.—*The Reaction between Picryl Chloride and Pyridine in Alcoholic Solution.*

By FRANCIS WILLIAM HODGES.

PICRYL chloride reacts very slowly with anhydrous alcohol even at 70°, but somewhat more rapidly with alcohol which has not been specially dried. It was anticipated that pyridine, by combining with the two acids formed by hydrolysis, would accelerate the reaction, and conductivity measurements with $M/40$- and $M/80$-solutions of pyridine and picryl chloride at 18·3° indicated a fairly rapid formation of ionised products. These alcoholic solutions slowly deposited lustrous, brown crystals, m. p. *ca.* 220°, and concentration of the remaining solution yielded pyridine picrate. The crystals were subsequently found to be picrylpyridinium picrate,  $C_5H_5N{<}{\begin{smallmatrix}C_6H_2(NO_2)_3\\ O{\cdot}C_6H_2(NO_2)_3\end{smallmatrix}}$. Analogous compounds have been prepared by Barnett and Cook (J., 1922, **121**, 792).

Since Wedekind (*Annalen*, 1902, **313**, 257) had isolated an additive compound of pyridine and picryl chloride, containing one molecule of each, from benzene solutions, it was thought that this compound might constitute an intermediate stage in the reaction under discussion. Wedekind's compound, m. p. 138°, was prepared, and its alcoholic solution slowly deposited crystals which were identical with those described above, although Wedekind had stated that the products of hydrolysis of his compound were pyridine picrate and hydrochloric acid.

On the assumption that this additive compound was the first intermediate product, the whole reaction was formulated as follows :

$$C_5H_5N + C_6H_2Cl(NO_2)_3 = C_5H_5N,C_6H_2Cl(NO_2)_3 \text{ (slow)} \quad . \quad . \quad (1)$$

$$C_5H_5N,C_6H_2Cl(NO_2)_3 + H_2O = C_5H_5N,C_6H_2(NO_2)_3{\cdot}OH + HCl \text{ (rapid)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$C_5H_5N + HCl = C_5H_5N,HCl \text{ (instantaneous)} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

these being accompanied by slow side reactions giving picrylpyridinium picrate and ethyl picrate (from the alcohol). The measurable reaction should therefore be bimolecular, and unimolecular with regard to each reactant.

The net effect of the above equations is

$$2C_5H_5N + C_6H_2Cl(NO_2)_3 + H_2O = C_5H_5N,HCl + C_5H_5N,C_6H_2(NO_2)_3{\cdot}OH.$$

Representing the initial concentrations of picryl chloride and pyridine as a and b, respectively, and the amount of pyridine picrate produced after time t as x, one has

$$dx/dt = k(b - 2x)(a - x) \quad . \quad . \quad . \quad . \quad (4)$$

The results obtained at 23·2° gave fair constancy for the velocity coefficients based on this assumption.

At higher temperatures, however, it is clear that this equation does not represent the reaction; in fact, at two different temperatures the concentration–time curves actually intersect. The initial velocity is greater for the higher temperature, but the velocity decreases more rapidly with time, so that, for a given degree of reaction above a certain value, the velocity is lower at the higher temperature. This result suggests an equilibrium reaction in which the equilibrium point is displaced with rising temperature in a direction which diminishes the concentration of one of the reactants in the principal reaction.

The assumption that pyridine in reaction (1) was replaced by pyridinium hydroxide, formed in relatively very small concentration by the mass-action equilibrium between pyridine and water, led to an equation similar in form to (4), but which demanded that the velocity should be directly proportional to the water concentration, and this was not in agreement with the experimental results (see Tables A, III and IV). A clue was sought in the colour changes which occur during the course of the reaction; the slow development of colour with the progress of the reaction, the fact that it was less pronounced at the higher temperatures, and its resemblance to that produced by Wedekind's additive compound in alcoholic solution, all pointed to the intermediate formation of this compound in equilibrium with pyridine and picryl chloride. Moreover, such a development of colour has been attributed to the formation of additive compounds of this nature by various workers (Burton and Kenner, J., 1921, ,**119** 1047; Kenner and Parkin, *ibid.*, 1920, **117**, 852; Sudborough and Picton, *ibid.*, 1906, **89**, 583; Hibbert and Sudborough, *ibid.*, 1903, **83**, 1336).

When Wedekind's compound was dissolved in cold alcohol, the concentration of the chloride ion *decreased* (Table B), whereas the addition of an alcoholic solution of picryl chloride caused an *increase*. These results point clearly to the chlorine in the additive compound being ionic, and to the slow dissociation of this substance into its constituents until an equilibrium point is reached, this equilibrium being displaced in the direction of less dissociation by the addition of picryl chloride.

The formation of pyridine picrate might take place (a) by the direct hydrolysis of the additive compound, or (b) by a side reaction between picryl chloride and water, pyridine acting as a catalyst.

The following facts supported the latter view:

1. The yield of ethyl picrate is considerably increased in the presence of pyridine and it seems reasonable to suppose that the corresponding reaction between picryl chloride and water would be similarly catalysed.

2. When the reaction is carried out in the presence of excess of water, the predominating reaction is that giving pyridine picrate.

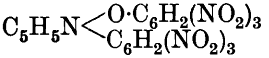
3. When the reaction was followed by the conductivity method, a perfectly smooth curve was obtained, whereas, with two consecutive reactions, of which the second results in the formation of hydrogen ions, there should be an induction period.

The course of the reaction is therefore assumed to be

$$C_5H_5N + C_6H_2Cl(NO_2)_3 \rightleftharpoons C_5H_5{:}NCl{\cdot}C_6H_2(NO_2)_3 \text{ (slow)} \quad . \quad . \quad (5)$$

$$C_5H_5N + C_6H_2Cl(NO_2)_3 + H_2O \longrightarrow C_5H_5{:}N(OH){\cdot}C_6H_2(NO_2)_3 + HCl \text{ (slow side reaction)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$C_5H_5{:}N(OH){\cdot}C_6H_2(NO_2)_3 + C_6H_2Cl(NO_2)_3 \longrightarrow$$



$$C_5H_5N{<}\begin{matrix} O{\cdot}C_6H_2(NO_2)_3 \\ C_6H_2(NO_2)_3 \end{matrix} + HCl \text{ (very slow)} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$C_6H_2Cl(NO_2)_3 + C_2H_5{\cdot}OH \longrightarrow C_6H_2(NO_2)_3{\cdot}O{\cdot}C_2H_5 + HCl \text{ (slow)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$C_5H_5N + HCl \longrightarrow C_5H_5N,HCl \text{ (instantaneous)} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Reaction (5) appears to be the main reaction and leads to the equation

$$dx/dt = k_1(a - x)(b - x) - k_2x \quad . \quad . \quad . \quad (10)$$

which, on integration, gives

$$k_1nt = \log_e (m - n)(m + n - 2x)/(m + n)(m - n - 2x),$$

where $m = a + b + K$ and $n^2 = (a + b + K)^2 - 4ab$, K being the equilibrium constant.

Reactions (7) and (8) each result in the disappearance of one equivalent of picryl chloride and one equivalent of pyridine, with the corresponding formation of one equivalent of hydrochloric acid, the only effect on the equilibrium being due to reduced ionisation of the additive compound and a consequent slight displacement in the direction of greater dissociation. Reaction (6) involves the disappearance of one equivalent of picryl chloride and two equivalents of pyridine, this again resulting in greater dissociation.

The combined effect of these side reactions would be expected to cause a reduced value for k_1 as the reaction proceeds, and this was actually the case. The effect is more marked at the higher concentrations, but is less marked in dried alcohol. It is seen from the tables that this hypothesis is fairly well substantiated by the results.

The addition of an increasing excess of water apparently causes reaction (6) to have greater influence and finally to predominate, no equilibrium point being obtainable (Tables A, III and IV). A similar effect is obtained with a large excess of pyridine. Evidence for this explanation was obtained when the reaction was carried out in bulk, and with a large excess of pyridine or of water. In both cases, a far higher yield of pyridine picrate was obtained.

EXPERIMENTAL.

A. *Preparation of Picrylpyridinium Picrate.*—Picryl chloride (6·19 g.) and pyridine (2 g.) were heated under reflux with 100 c.c. of absolute alcohol for 4 hours. On cooling, 4·4 g. of lustrous, brown crystals were deposited. This compound was insoluble in alcohol, glacial acetic acid, benzene, ether, or light petroleum, but soluble in acetone, pyridine, or glycerol, and moderately easily soluble in nitrobenzene. It dissolved in 50% aqueous alcohol, from which it separated in golden-yellow crystals, m. p. 226° (decomp.) (Found: C, 39·5; H, 2·3; N, 18·8; *M*, in acetone, 521; *M*, in nitrobenzene, 519. Calc.: C, 39·4; H, 1·8; N, 18·9%; *M*, 519). With potash, it gives pyridine on heating.

Further proof of the composition was obtained by grinding picrylpyridinium chloride and sodium picrate under acetone. The residue after evaporation was boiled with water and filtered. The brown residue, m. p. 223°, was identical with the compound already described.

B. *Isolation of Other Products of the Reaction.*—After the removal of picrylpyridinium picrate from the main reaction mixture, small quantities of pyridine picrate and ethyl picrate were obtained. A solution of 12·4 g. of picryl chloride and 4 g. of pyridine in 100 c.c. of absolute alcohol was boiled under reflux for 1 hour. The yield was about 1 g. of picrylpyridinium picrate, and, on concentration of the filtrate, 6 g. of the additive compound, which, on being boiled with excess of alcohol, gave picrylpyridinium picrate. Similar treatment with 50% aqueous alcohol gave chiefly pyridine picrate.

Repetition of the first experiment, excess of pyridine or equivalent quantities in 75% aqueous alcohol being used, gave pyridine picrate as the main product.

C. *Velocity Measurements.*—At the outset the following method was employed for investigating the rate of formation of the additive compound. Measured quantities of the reaction mixture were transferred at intervals to a flask containing a known excess of nitric acid. Excess of a solution of potassium iodide and iodate in the proportions required by the equation $5KI + KIO_3 + 6HNO_3 = 6KNO_3 + 3H_2O + 3I_2$ was then added, and the liberated iodine was titrated with sodium thiosulphate. Although the method was not considered sufficiently accurate for velocity measurements, it served to show that there was a small gradual decrease in the amount of pyridine present, so that the first reaction, resulting in the formation of picrylpyridinium chloride, was comparatively slow.

Rheinlander (J., 1923, **123**, 3099), investigating the reactions between picryl halogen compounds and aniline hydrochloride, and other reactions of a similar nature, made use of the method described below. This was found to be more satisfactory and was employed throughout.

Measured quantities (10 c.c.) of the reaction mixture were transferred at intervals to a separator containing 20 c.c. of benzene, 10 c.c. of dilute nitric acid, and 20 c.c. of $N/80$-silver nitrate. Vigorous shaking resulted in the absorption of the coloured compounds by the benzene layer; the greater part of the silver chloride remained at the junction of the two liquids and there was no need to filter it. The aqueous layer was separated, united with the washings from the benzene layer, and titrated with $N/80$-potassium thiocyanate.

Variations in the concentrations were limited by the impossibility of making up cold alcoholic solutions of picryl chloride stronger than $M/20$.

The unit employed throughout is the equivalent of 1 c.c. of $M/40$-solution for 10 c.c., *i.e.*, one four-hundredth of a mol. per litre.

When the reaction was carried on for a sufficient length of time at 23·2° in dry or absolute alcohol, a point was reached after about 3 hours at which the titrations were practically constant. In most cases, the equilibrium point was obtained by taking measurements 10 hours after mixing. Beyond this stage, a very slow formation of chloride ion could be observed from titrations taken at daily intervals.

The equilibrium constant $K = k_2/k_1$ [see (10)] was calculated in the forward reaction from the equation

$$K = (a - x)(b - x)/x,$$

the mean value obtained being 2·28 at 23·2°.

Measurements were also made of the rate of decomposition of picrylpyridinium chloride. Only very dilute solutions could be used owing to the relative insolubility of this compound in cold alcohol. Calculation of the initial velocity showed fairly good agreement with the result obtained for k_2 from the equilibrium constant. From the reverse reaction

$$K = [\text{Pyridine}][\text{Picryl chloride}]/[\text{Picrylpyridinium chloride}]$$

the mean value at 23·2° was 2·20.

From the initial velocity coefficients obtained from the opposing reactions, calculated from the simple bimolecular and unimolecular formulæ, respectively, one finds, *e.g.*,

$$K = k_2/k_1 = 0{\cdot}00774/0{\cdot}00375 = 2{\cdot}07,$$

the average value being 2·05.

Owing to considerations of space, only the necessary typical series of measurements are given and the remainder are summarised in Table C. Time is in minutes in all cases.

TABLES A.

Reaction between Pyridine and Picryl Chloride.

I.

$a = 5$, $b = 7{\cdot}5$. Solvent : Absolute alcohol. Temperature : 23·2°.

t.	x.	$k_1 \times 10^5$.
11	1·14	368
20	1·76	369
30	2·23	362
40	2·53	375
60	2·83	348
90	3·14	353
	Mean	364

II.

$a = 5$, $b = 5$. Solvent : Absolute alcohol. Temperature : 23·2°.

t.	x.	$k_1 \times 10^5$.
10	0·79	361
20	1·23	359
30	1·58	359
40	1·80	347
60	2·13	348
90	2·32	311
600	2·60	—
	Mean	329

III.

$a = 5$, $b = 5$. Solvent : Dried alcohol + 2 c.c. of water in 100 c.c. Temperature : 23·2°.

t.	x.	$k_1 \times 10^5$.	$^*k \times 10^5$.
10	0·81	406	422
20	1·29	389	416
30	1·62	376	428
60	2·20	385	469
100	2·49	—	—
	Mean	394	439

IV.

$a = 5$, $b = 5$. Solvent : Dried alcohol + 6 c.c. of water in 100 c.c. Temperature : 23·2°.

t.	x.	$^*k \times 10^5$.
10	1·01	530
20	1·49	552
33	1·93	593
43	2·11	588
600	3·90	—
	Mean	566

* Calculated from the integrated form of equation (4).

V.

$a = 5$, $b = 5$. Solvent : Absolute alcohol. Temperature : 33·3°.

t.	x.	$k_1 \times 10^5$.
10	1·21	775
20	1·75	777
30	1·94	712
40	2·04	665
250	2·22	—
	Mean	732

VI.

$a = 5$, $b = 5$. Solvent : Absolute alcohol. Temperature : 49·1°.

t.	x.	$k_1 \times 10^5$.
10	1·45	1480
20	1·60	1290
30	1·63	1060
65	1·65	—
	Mean	1320

An experiment at 39·7° gave $k_1 \times 10^5 = 827$.

TABLE B.

Decomposition of Picrylpyridinium Chloride.

Solvent : Absolute alcohol. Temperature : 23·2°.

t	0	25	70	300
c	3·52	2·90	2·35	1·60

This gives an initial value for $k_2 \times 10^5$ of 751, and a second experiment, using an initial concentration of 2·21, gave 786.

TABLE C.

(Temperature throughout, 23·2°. The solvent was ordinary alcohol in all cases except that marked †, in which anhydrous alcohol was used.)

		$k_1 \times 10^5$.				$k_1 \times 10^5$.	
a.	*b.*	Range.	Mean.	*a.*	*b.*	Range.	Mean.
4·85	5·00	339—299	315	10·00	7·58	314—269	290
9·90	5·00	303—259	282	†5·00	5·00	355—301	312
4·70	10·00	308—263	286	10·00	10·00	326—257	300
5·00	5·05	316—274	309	7·50	7·40	337—274	312
7·50	7·58	321—250	288	7·50	5·00	310—271	285
7·50	10·10	362—279	321	4·93	7·40	342—291	331
4·00	20·20	354—315	323*				

* Based on integrated form of equation (4).

Summary.

1. The reaction between picryl chloride and pyridine in alcoholic solution is bimolecular and results in the slow formation of an ionised additive compound, picrylpyridinium chloride. The quantity of this compound produced depends on the concentration of the reactants and on the temperature.
2. The equilibrium reaction is accompanied by slow side reactions in which pyridine picrate and ethyl picrate are produced, the former being considerably accelerated by the presence of water.
3. A very slow reaction—only apparent after a few days—takes place between picryl chloride and pyridine picrate, with the result that picrylpyridinium picrate crystallises from the solution.
4. The evidence adduced for the formation of an ionised additive compound points to the probability of the formation of similar substances when picryl halogen compounds react with other aromatic amino-bases, at any rate as a preliminary to other reactions which may take place.

The author wishes to express his indebtedness to the authorities of the Chelsea Polytechnic for the facilities enjoyed, and particularly to Dr. J. C. Crocker for his direction and advice.

CHELSEA POLYTECHNIC, S.W. [*Received, May* 31*st*, 1926.]