

529. The Kinetics of the Reaction between Methyl Iodide and Potassium Cyanide in Aqueous Solution.

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The reaction between methyl iodide and potassium cyanide in aqueous solution is shown to be irreversible, bimolecular, and free from complications. The Arrhenius equation is $\ln k_2$ (l. mole⁻¹ sec.⁻¹) = 26.284 - 19,990/RT.

Experimental.—The kinetics of formation of nitriles from alkyl halides and potassium cyanide in aqueous solution have not hitherto been studied. The reaction $\text{CH}_3\text{I} + \text{CN}^- \longrightarrow \text{CH}_3\text{CN} + \text{I}^-$ has now been studied in aqueous solution in the absence of the vapour in the new reaction vessel.¹ Solutions of methyl iodide were made up in conductivity water that had been freed from dissolved gases; known volumes of the solution, about 475 ml., were then kept in the thermostat, and about 25 ml. of a standard solution of potassium cyanide were added from a burette to make the total volume of solution exactly 500 ml. The solutions were thoroughly mixed and immediately transferred to the reaction vessel. Samples were removed at regular intervals and immediately analysed for cyanide or iodide ion. The temperature of the system remained constant to within 0.01° c in individual runs, and to within 0.03° c in different runs.

Methyl iodide was purified by the same method and to the same standard as that used by earlier workers in this Department. Distilled water which had been passed through Amberlite ion-exchange and thoroughly out-gassed by vigorous boiling under reduced pressure was used in making up the solutions required for the kinetic studies. "AnalaR" (B.D.H) potassium cyanide was shaken with ethyl alcohol, washed with ether, and dried in a vacuum desiccator during the initial work, until it was confirmed that the use of the same material without further purification had no effect on the rate constant.

Analytical Methods.—Samples of the solution were analysed for both cyanide and iodide ions by standard argentometric methods. The former was measured by Liebig and Denigés's method under the conditions recommended by Kolthoff,³ the titration being sensitive to within 0.05 ml. of 0.01N-silver nitrate. Iodide ion was estimated after removing free cyanide as a soluble cyanohydrin with formalin, as described by Kolthoff and Stenger.⁴

The initial concentration of methyl iodide was measured by determining the iodide ion liberated when samples of the reaction mixture were allowed to react to completion in Pyrex ampoules in an oven at 100°. It was also necessary to estimate the concentration of acetonitrile at the end of a run to discover how much methyl isocyanide, if any, had been formed. This was quite easily done, since it is stable to alkali, while acetonitrile is readily hydrolysed, giving ammonia as the only volatile product.

Cyanide ion, which also gives ammonia on hydrolysis, was removed from the samples, which had been allowed to react to completion in the thermostat, by titration with silver nitrate to a clear point. After thorough washing of the precipitate, the filtrate and washings were gently refluxed with 5N-sodium hydroxide for 2 hr., and then vigorously boiled for 30 min. to transfer all the liberated ammonia into the absorption solution of 4% boric acid. The absorbed ammonia was then titrated against standard hydrochloric acid, methyl red being used as indicator. The

TABLE I. Estimated amounts of acetonitrile formed.

By ammonia liberated in hydrolysis (mmoles/l.)	35.50	35.55
By iodide ion liberated in the reaction (mmoles/l.)	34.95	35.05
Blank (mmole/l.)	0.75	0.60

difference between the amount of acetonitrile formed and the amount of methyl iodide consumed was negligible, *i.e.*, comparable in magnitude with the results of blank experiments carried out on solutions containing cyanide ion but no acetonitrile; hence no isocyanide is formed under these conditions (see Table I).

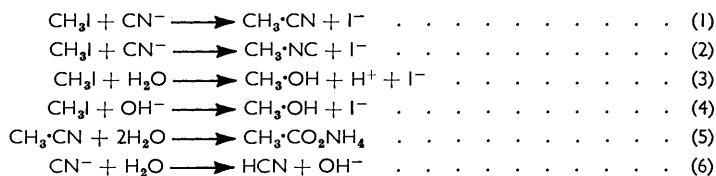
¹ Farhat-Aziz and Moelwyn-Hughes, preceding paper.

² Fahim and Moelwyn-Hughes, *J.*, 1956, **214**, 1034.

³ Kolthoff and Stenger, "Volumetric Analysis," Interscience, New York, 2nd Edn., 1947, Vol. 2, pp. 282—283.

⁴ *Op. cit.*, pp. 266—267.

Kinetic Scheme.—In principle, at least six reactions can take place:



Reaction (1) goes to completion, and reaction (2) does not occur under the conditions employed. The known rates of reactions (3) and (4) as measured by Moelwyn-Hughes⁵ are so much less than the rate of reaction (1) as to be negligible in this study; this fact is consistent with the impossibility of differentiating between the constants calculated from the rate of liberation of iodide ion and those calculated from the rate of consumption of cyanide ion (see Table 2).

The hydrolysis of acetonitrile, reaction (5), would not affect the kinetic analysis, but might have affected the static analysis of the product. Separate experiments with aqueous solutions of acetonitrile alone, however, showed that the rate of hydrolysis was extremely slow, even at 85°, and of no significance in the temperature range employed. The hydrolysis of the cyanide ion, reaction (6), may well be so rapid as to establish equilibrium throughout. Whether this is true or not, a solution containing 150 mmoles/l. of potassium cyanide showed that the extent of hydrolysis was less than 1%. For this reason a correction was not applied for the difference between the concentrations of total cyanide and of cyanide ion.

Results.—In runs followed up to 90% completion the rate constants, as calculated from the ordinary equation for an irreversible second-order reaction, showed no tendency to drift. No variation of rate constant with initial concentration of potassium cyanide was found when this

TABLE 2.

Run at 41.24° C = 314.40° K; $a = [\text{CH}_3\text{I}]_0 = 25.77$ mmoles/l.; $b = [\text{CN}^-]_0 = 39.10$ mmoles/l.; $k_2 = 3.37 \times 10^{-3}$ l. mole⁻¹ sec.⁻¹. Unit of concentration = mmole/l.

<i>t</i> (min.)	[CN ⁻] obs.	[I ⁻] obs.	[CN ⁻] calc.	[I ⁻] calc.	<i>t</i> (min.)	[CN ⁻] obs.	[I ⁻] obs.	[CN ⁻] calc.	[I ⁻] calc.
0.0	39.10	—	39.10	0.0	210.0	21.55	—	21.32	17.78
15.5	—	2.65	36.45	2.89	240.0	—	18.74	20.38	18.72
36.0	33.05	—	33.16	5.94	270.0	19.65	—	19.58	19.52
55.0	—	8.08	30.87	8.23	300.0	—	20.30	18.82	20.28
75.0	28.90	—	28.88	10.22	325.0	18.45	—	18.39	20.65
95.0	—	11.83	27.25	11.87	350.0	—	21.15	17.94	21.16
116.0	25.60	—	25.74	13.36	386.0	17.60	—	17.39	21.71
135.0	—	14.47	24.62	14.48	421.0	—	22.20	16.93	22.17
155.0	23.70	—	23.57	15.53	450.0	16.60	—	16.59	22.51
180.0	—	16.63	22.46	16.64	∞	—	25.77	13.33	25.77

TABLE 3. *The effect on the rate constant at 318.46° K of varying the potassium cyanide concentration and of adding potassium nitrate.*

[KCN] (mmoles/l.)	30.22	49.92	50.0	50.0	99.54	50.0
[KNO ₃] (mmoles/l.)	0	0	0	10	0	100
10 ³ k ₂ (l. mole ⁻¹ sec. ⁻¹)	5.02	5.07	4.92	5.15	4.94	5.09

TABLE 4.

<i>T</i> (°K)	293.26	300.05	305.32	309.87	314.40	318.46	323.00	327.43
10 ⁴ k ₂ (l. mole ⁻¹ sec. ⁻¹), obs.	3.27	7.21	13.3	21.7	33.8	50.3	82.2	127.0
„ „ calc.	3.36	7.44	13.1	21.6	33.9	51.2	79.7	122.0

concentration was varied from 30 to 150 mmoles/l., nor did the addition of up to 100 mmoles/l. of potassium nitrate produce any systematic change in the rate of reaction. A specimen set of data for one run, analysed for iodide and cyanide ions alternately, is shown in Table 2, together

⁵ *Proc. Roy. Soc., A*, **220**, 286—296; 1949, *A*, **196**, 540.

with the calculated values of the two ionic concentrations at each point. The influence of the initial concentrations is shown in Table 3. The velocity coefficients remained constant to within 2% from run to run. Values of the rate constant, k_2 , at different temperatures have been fitted by the method of least squares to a straight-line plot of $\log_{10}k_2$ against $1/T$. Table 4 gives a comparison of the mean measured values of k_2 with those calculated from the Arrhenius equation. Observed and calculated values agree to within $\pm 4\%$. The probable error in the apparent energy of activation is ± 70 cal./mole.

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