CXXII.—*Termolecular Reactions. Reduction of Silver Acetate by Sodium Formate.*

By ALEXANDER COUTIE.

IN a recent investigation of the reaction occurring between formaldehyde and bases, the author had occasion to make use of various velocity equations, in an attempt to settle the order of reaction. A comparison of the formulæ employed by other experimenters, working along similar lines, showed that in many cases these were in error. This can best be explained by reference to the fundamental differential equation, which is readily arrived at in the following way.

Multimolecular chemical reactions are of two types. The first class consists of those in which the participation of one molecule of each of n different substances, all originally of the same molar concentration, is necessary and sufficient for the occurrence of the change. The differential equation assumes the form

$$-dC/dt = kC^n \qquad (1)$$

(All concentrations in this section may be taken as measured in g.-mols. per litre.) The other class is much more general, and includes those reactions in which the n molecules, taking part in the change, are not all different. If m_1 molecules of substance A, reacting with initial concentration C_1, disappear for every m_2 molecules of substance B—of original concentration C_2—and so on

$$-dC/dt = kC_1^{m_1}C_2^{m_2}C_3^{m_3} \quad . \quad . \quad . \qquad (2)$$

where $m_1 + m_2 + m_3 + \ldots = n$.

This equation can be put in a more useful form. If several substances A, B, C, . . ., with initial concentrations a, b, c, . . ., take part in a simple reaction, undisturbed by any simultaneous or secondary changes, and if l, m, n, . . . are the numbers of molecules of A, B, C, . . . which must react simultaneously before the change considered can take place, then, when x is the actual fall in concentration, in time t, of a substance of which only one molecule is necessary for the progress of the reaction,

$$dx/dt = k(a - lx)^l\,(b - mx)^m(c - nx)^n \quad . \quad . \qquad (3)$$

the number of factors being equal to the number of different substances taking part in the reaction. A similar equation has been given by Wegscheider (*Z. physikal. Chem.*, 1900, **35**, 513).

From this general equation can be deduced all the ordinary unimolecular, bimolecular, etc., velocity formulæ, but in certain cases it leads to forms at variance with those already mentioned as being employed by a number of investigators. The disputed equations refer to reactions in which two or more molecules of at least one of the substances present are necessary for the progress of the change, *i.e.*, when one or more of the quantities l, m, n, . . . in equation (3) is greater than unity. Applied to termolecular reactions of this type, as being those with which the author was chiefly concerned, the general equation gives the following formulæ.

Termolecular.—When a change takes place involving the interaction of three molecules of A, the sole reactant present, equation (3) reduces to

$$dx/dt = k(a - 3x)^3 \qquad (4)$$

but when two molecular species A and B take part—their initial concentrations being a and b, respectively—and two molecules of B react with one of A, then

$$dx/dt = k(a - x)(b - 2x)^2 \qquad (5)$$

In a formula such as (4)—where a is the total initial concentration of the reactant of which three molecules take part in the change, and x is the reduction in concentration, in time t, due to *each* molecule reacting—it is quite allowable, if absolute values of the velocity coefficient are not required, to make the substitution $x_1 = 3x$, whence

$$dx_1/dt = k_1(a - x_1)^3 \qquad (6)$$

and $k_1 = 3k$. It is obviously not justifiable to make such a substitution in one term of a differential equation and not in another. For example, the values of k obtained from equation (5) are not constant multiples of those derived from the form

$$dx/dt = k(a - x)(b - x)^2 \qquad (7)$$

It is in this virtual neglect of the coefficients of x that the experimenters already referred to were in error.

For instance, Noyes and Cottle (*Z. physikal. Chem.*, 1898, **27**, 579; *J. Amer. Chem. Soc.*, 1899, **21**, 250) employ formula (7) in their study of the reaction between silver acetate and sodium formate, which may be represented by the equation

$$2CH_3{\cdot}CO_2Ag + H{\cdot}CO_2Na = 2Ag + CO_2 + CH_3{\cdot}CO_2H + CH_3{\cdot}CO_2Na.$$

They state that in this formula a and b are the initial concentrations of sodium formate and silver acetate, respectively, and x the measured fall in concentration of the latter substance. Although the concentration of the silver acetate falls at twice the rate of that of the sodium formate, their formula does not show this. Moreover, their formula is restricted in its application when a is less than b, in which case it can only be employed as long as x is less than a, *i.e.*, during the first half of an experiment. Noyes and Cottle continued their work past the point of half-decomposition in all experiments except, unfortunately, those to which this applies. The formula which they should have used is evidently

$$dx/dt = k(a - x/2)(b - x)^2 \qquad (8)$$

This is identical in form with equation (5).

The use of erroneous formulæ of the above type by several workers is possibly due to their having accepted without question or appropriate modification those given by Ostwald ("Lehrbuch der allgemeinen Chemie," 1887, II, 615—634) and integrated by Fuhrmann (*Z. physikal. Chem.*, 1889, **4**, 89), which are all of a simple and straightforward nature.

Reduction of Silver Acetate by Sodium Formate.

Since the days of van 't Hoff it has been recognised that reactions of order higher than the second are few in number, and certain examples brought forward from time to time have been severely criticised and shown to afford little or no evidence in favour of such changes. A reaction frequently quoted as being one of the most thoroughly investigated and typical examples of a termolecular transformation, and one which has never been seriously called in question, is that under discussion.

In their investigation of this reaction Noyes and Cottle (*loc. cit.*)

obtained velocity coefficients by the use of an erroneous formula (compare previous page).

Substitution of their data in the correct equation gives values which are far from constant, as can be seen from the following example.

$$a = [\mathrm{H{\cdot}CO_2Na}] = 0{\cdot}050\,N;\ b = [\mathrm{CH_3{\cdot}CO_2Ag}] = 0{\cdot}100\,N.$$

t (mins.).	$b - x$.	k_3 (Noyes and Cottle).	k_3 (corrected).
2	0·08103	30·0	26·2
4	0·07180	30·2	23·5
7	0·06395	31·2	20·6
11	0·05920	29·7	16·9
16	0·05625	28·0	13·5

These facts suggested inaccuracy in their experimental work, which, although correct in outline, may be criticised on one or two points.

To begin with a matter of minor importance, the temperature at which they carried out their experiments was the boiling point of water under the atmospheric pressure, and although, owing to the short duration of a single experiment, the error thus introduced would not be appreciable except in the comparison of the velocity coefficients of the various experiments, yet an ordinary change in pressure might result in an error of 10% in the coefficients.

Whilst excessively slow reactions cannot be relied on to give satisfactory results, it must also be recognised that very quick reactions are subject to great experimental error. There was no need for these investigators to perform their experiments at 100°, with consequent times of half-decomposition of the order of a few minutes; a temperature of 75° gives a velocity at once convenient from the point of view of the time required and capable of accurate measurement.

The method of titration employed by Noyes and Cottle is liable to slight inaccuracy on account of difficulties in the quantitative filtration of the finely-divided suspension resulting from the addition of the reaction mixture to the thiocyanate solution. The author considers that the error thus introduced may account, at least in part, for the apparently abnormal data obtained by these investigators.

It need scarcely be emphasised that their experiments afford absolutely no proof that the reaction is of the third order.

Re-investigation of the Reaction.

The procedure was as follows. Solutions of the two salts at the same temperature (74·97° ± 0·02°) were rapidly mixed in such proportions that the resulting solution was of a known concentration with regard to each. One solution was placed in a boiling tube,

A, which was fitted with a syphon tube, leading to the bottom of a similar vessel, B, containing the other solution, and also with an inlet tube through which air could be passed to force the liquid from A into B. The apparatus was standardised in order to allow for the small quantity of solution unavoidably remaining in vessel A and in the syphon tube. At a definite time after the two had been mixed and thoroughly agitated by a current of air, an analysis sample of about 10 c.c. was withdrawn, and rapidly cooled in ice. As it was essential to remove the insoluble products of reduction before titration, a very small filter-paper was well washed with 2 c.c. of the cooled solution and the remainder was filtered through it. Attention to the size of paper and the preliminary washing was necessary to reduce the loss due to adsorption of silver salt during filtration. 5 C.c. of the filtered solution were titrated with potassium thiocyanate, ferric alum being used as indicator, the accuracy being 0·02 c.c. Consideration was given to various possible sources of error, such as the colloidal products of reduction not retained by the filter and dissolved by the nitric acid in the indicator solution, and the change in normality of the solutions on heating to 75°.

Silver acetate and sodium formate give alkaline solutions, and as the change to an acid reaction, which takes place during the course of an experiment, might have introduced disturbances, experiments were performed in which varying amounts of acetic acid were added initially. Since the results with and without acid were sensibly the same, this precaution was not considered essential.

The tables of results give the velocity coefficients calculated from the correct formula in the column headed k (correct), and, for comparison, those obtained by the use of Noyes and Cottle's formula under the heading k(N. and C.). The correct formula, $dx/dt = k(a - x/2)(b - x)^2$, where a and b are the total initial normalities of sodium formate and silver acetate, respectively, and x is the fall in normality of silver acetate in time t, gives on integration

$$k = \frac{2}{(2a - b)^2 t}\left\{\frac{(2a - b)x}{b(b - x)} + \log_e \frac{2a(b - x)}{b(2a - x)}\right\},$$

while Noyes and Cottle's equation $dx/dt = k(a - x)(b - x)^2$, where a, b and x have the same significance as above, gives

$$k = \frac{1}{(a - b)^2 t}\left\{\frac{(a - b)x}{b(b - x)} + \log_e \frac{a(b - x)}{b(a - x)}\right\}.$$

The values of x given are calculated from the mean titration figures of from three to six experiments for each concentration. The accuracy obtained can best be shown by comparing the figures for a single concentration : t is the time in minutes, s the values (c.c.) from a single experiment, and r the average of three experiments.

$$[HCO_2Na] = 0{\cdot}05N; \quad [CH_3{\cdot}CO_2Ag] = 0{\cdot}05N.$$

t	20	40	70	100	160	240
s	8·98	7·19	5·58	4·55	3·28	2·37
r	8·97	7·19	5·59	4·56	3·28	2·41

Tables of Results.

$$a = 0{\cdot}100; \quad b = 0{\cdot}050.$$

t (mins.).	x.	k (corr.).	k (N. and C.).	t (mins.).	x.	k (corr.).	k (N. and C.).
20	0·0218	8·28	8·92	100	0·0395	8·84	10·81
40	0·0299	8·26	9·32	160	0·0433	9·79	12·55
60	0·0344	8·36	9·75	240	0·0460	11·94	15·98

The initial concentrations and the ranges of k (corr.) and k (N. and C.) in three similar experiments were :

a = 0·050, b = 0·050, k (corr.) = 8·45—10·25, k (N. and C.) = 9·40—21·77
0·050, 0·025, 9·49—11·46, 9·75—13·73
0·025, 0·050, 8·61— 9·48, 9·64—32·52*

* These figures refer only to the first half of the reaction, as Noyes and Cottle's formula cannot be applied after the point of half-decomposition (compare p. 889).

Values calculated from the bimolecular formula are in all cases far from constant.

The following table gives the velocity coefficients, calculated from the correct formula, corresponding to the times of half-decomposition.

a	0·100	0·050	0·050	0·025
b	0·050	0·050	0·025	0·050
k	8·3	8·5	9·7	9·4

These figures indicate that, whilst the reduction of a silver salt in dilute solution by a formate is not a rigid termolecular reaction, yet, both from the point of view of the constancy of the values in any one experiment and from the slight variation in the magnitude of the constant with change in initial concentration of the reactants, it appears that the reaction is essentially one of the third order.

Summary.

The correct velocity equation has been deduced for those termolecular reactions in which two molecules of one of the reactants take part in the change.

Definite proof has been advanced that the reduction of silver acetate by sodium formate is essentially a reaction of the third order.

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