endotherm verläuft. Dabei wird der Bereich des exothermen Mischens ($\overline{H}^E < 0$) mit zunehmender Temperatur immer kleiner.

Bei Vergleich mit den älteren Daten[1,2] ergibt sich gute Übereinstimmung im Konzentrationsintervall $0 < x < 0{,}6$.

Kalorimetrische Daten aus der Literatur[1,2,5] über flüssige Systeme des Typs Wasser + Monocarbonsäure zeigen, daß $\overline{H}^E$ für Wasser + Ameisensäure stets negativ, für Wasser + Propionsäure und Wasser + Buttersäure aber immer positiv ist. Das System Wasser + Essigsäure nimmt also eine Zwischenstellung ein.

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[1] M. A. Faucon, Ann. Chim. Phys. **8**, 19, 70 [1910].

[2] C. Sandonnini, Atti Accad. Lincei **22**, 1, 20 [1913].

[3] H. Grosse-Wortmann, Dissertation, Universität Göttingen 1964.

[4] P. Steinmetz, Dissertation, Rheinisch-Westfälische Technische Hochschule Aachen 1972.

[5] A. N. Campbell, J. Amer. Chem. Soc. **59**, 2, 2481 [1937].

Kinetics of Ester-interchange between Methyl Acetate and Ethanol

T. S. Rao and B. R. Gandhe

Department of Chemistry, University of Poona
Poona-7 (India)

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Kinetics of ester-interchange between methyl acetate and ethanol has been studied in the range 80—105°, using gas chromatographic technique. The reaction is of the second order, and the specific reaction rate is $29.6 \cdot 10^{-8}$ l/mole-sec at 105°. The energy of activation is 16.7 kcal/mole and the entropy of activation is −44.3 cal/mole-deg.

Ester-interchange is usually a very slow reaction, catalysed either by acid or base[1] and a study of its kinetics is often tedious because of the difficulty of quantitative estimation of low concentrations of the products. Hence it is not surprising that kinetic data on ester-interchange are scarce[2,3]. The high resolving power and extreme sensitivity of gas chromatography enable minute amounts of reaction products to be estimated, so that the kinetics of even very slow reactions can be studied[4–6]. Hence the technique has been adopted to study the kinetics of a typical ester-interchange, namely the one between methyl acetate and ethanol, catalysed by sodium carbonate, the products being ethyl acetate and methanol.

In each of several Pyrex test tubes 4 ml of an equimolar mixture of methyl acetate and ethanol and 2 g of anhydrous sodium carbonate (80 – 100 mesh) were placed. The tubes were sealed off and placed in a thermostat at 80°. After known intervals of time one tube at a time was withdrawn, cooled rapidly to room temperature, and cut open. The reaction mixture was filtered and analysed using a Beckman Gas Chromatograph GC-2. Nitrogen was the carrier gas at an inlet pressure of 2 kg/cm² and a flow rate of 40 ml/min. The column was a copper tube (2 m long, 6 mm i. d.) packed with Celite (40 – 60 mesh), loaded with 20% Carbowax 4000. The detector was a thermal conductivity cell with a filament current of 150 mA. The temperature of the column and the detector was 70°. The chromatograms were recorded on Bristol Dynamaster Recorder with a sensitivity of 1 mV for full scale deflection.

Each time 5 μl of the reaction mixture were injected into the GC column and the peaks of the products were recorded. These peaks were evaluated from a calibration curve obtained by recording the peaks for different volumes of an equimolar mixture of ethyl acetate and methanol.

If y μl of the products were formed after a given time, their concentration (x) was given by

$$x = (y/5)/0.1382 \text{ moles/l},$$

since the volume of a mixture of a mole each of ethyl acetate and methanol was 138.2 ml, and 5 μl of the reaction mixture were injected into the column. Further, in an equimolar mixture of the reactants the concentration (a) of each was $a = 7.26$ moles/l, since 137.8 ml was the volume of a mixture of a mole each of methyl acetate and ethanol. A plot of $(1/a - x)$ versus time was linear (Fig. 1) implying that the reaction was of the second order. The slope of the plot was the specific reaction rate (k).

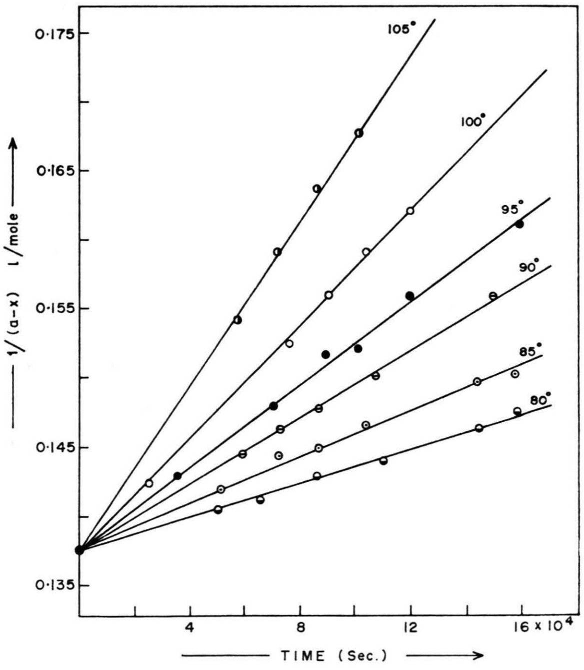

Fig. 1. Kinetics of ester-interchange between methyl acetate and ethanol.

Table 1. Kinetics of ester-interchange between methyl acetate and ethanol. Vairation of specific reaction rate (k) with temperature.

Temperature (°C)	80	85	90	95	100	105
Specific reaction rate k (10^{-8} l/mole-sec)	5.91	8.62	12.3	15.0	21.1	29.6

The experiment was repeated at several temperatures in the range 80 – 105° (Ref. Table 1).

From the results the energy of activation was evaluated to be 16.7 kcal/mole and the entropy of activation to be – 44.3 cal/deg. mole.

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[1] J. D. ROBERTS and M. C. CASERIO, Basic Principles of Organic Chemistry, W. A. Benjamin, Inc., New York 1965, p. 532.

[2] A. N. PUDOVIK, R. A. CHERKASOV, and R. M. KONDRATEVA, Vysokomol. Soedin, Ser. A **9** (5), 1118 [1967].

[3] J. HRIVNAK, Z. VESELA, E. SOHLER, and J. DRUBEK, Chem. Prumysl. **15** (1), 7 [1965].

[4] H. J. ARNIKAR, T. S. RAO, and A. A. BODHE, J. Chromatog. **47**, 265 [1970].

[5] P. LORRAINE, P. ROWLAND, MACK, H. CHARLES, COLL, and E. EMERY, J. Gas Chromatog. **6** (3), 173 [1968].

[6] V. PETERKA, ZBIROVSKY, and MIROSLAV, Collect. Czech. Chem. Commun. **35** (3), 1010 [1970].

Excitation of N_2^+ by Vibrating Nitrogen Molecules

R. J. ALDERSON * and B. BROCKLEHURST **

Chemistry Department, Sheffield University, U.K.

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Flowing nitrogen gas, bombarded by 50 keV electrons, emits the first negative and second positive bands. Operation of a microwave discharge upstream enhances the former, but not the latter: this is shown to be due to conversion of vibrational excitation in N_2 into electronic excitation in N_2^+.

OLDENBERG[1] has reviewed excitation processes in nitrogen discharges and afterglows. The B → X, first negative bands of N_2^+ are directly excited from N_2 in the negative glow of a d.c. discharge (or when nitrogen is bombarded by past particles). In low frequency[2] and microwave discharges[3] there is evidence of indirect excitation; the best evidence of such processes comes from a study of the pink afterglow (P.A.) by BRÖMER and DÖBLER[4], who showed that the population rate of $N_2^+(B)$ is greater than the ionisation rate. Some plausible processes are:

$$N_2^+(X) + N_2^\dagger \rightarrow N_2^+(B) + N_2\,, \tag{1}$$

$$N_2^+(X) + e \rightarrow N_2^+(B) + e\,, \tag{2}$$

$$N_2^+(X) + N_2^m \rightarrow N_2^+(B) + N_2\,, \tag{3}$$

$$N + N_3^+ \rightarrow N_2^+(B) + N_2\,. \tag{4}$$

N_2^m, $N_2^\dagger$ represent metastable, electronically-excited and ground state, vibrationally excited N_2, respectively. The processes may well be complex; e. g. (1) may involve step-wise vibrational excitation of N_2^+ followed by collisional conversion between the X, A and B states.

Interconversion of nitrogen ions (N^+, N_2^+, N_3^+, N_4^+) does occur in nitrogen afterglows[5,6] but there is no evidence that (4) leads to excitation of N_2^+; it appears to be ruled out by the absence of N_2^+ emission from an auxiliary discharge in the Lewis-Rayleigh afterglow[3]. The other three processes are less easily distinguished because of the case of exchange of energy between these species. For example, in afterglows, process (5)[7] leads to rapid equilibration between the energy distributions of $N_2^\dagger$ and electrons:

$$N_2^\dagger + e \rightleftharpoons N_2 + e\,, \tag{5}$$

i. e. (1) is not easily distinguished from (5) followed by (2).

The study[8] of electron beam excitation of nitrogen has therefore been extended to gas flowing from a microwave discharge: this is known to contain high concentrations of $N_2^\dagger$ [9]. Though still complicated, the excitation processes are likely to be simpler than in the discharge or the P.A.

"Oxygen-free" nitrgen (British Oxygen Gases) was used: ready production of the P.A. indicated adequate purity. Before reaching the electron-beam cell, the gas flowed through a straight silica tube, 10 mm i. d.; the position of the microwave cavity could be adjusted along this tube to give distances of 15 – 120 cm between it and the cell. Electrons accelerated to 50 keV *in vacuo* passed through a thin aluminum foil[8] into the nitrogen stream at right angles to the flow. Successful preliminary experiments were carried out in a pyrex cell similar to that used before[8]: it was a cylinder, 3 cm in diameter, the flowing gas entering and leaving through 1 cm diameter side tubes; however, the flow pattern in the cell was uncertain and the P.A. often appeared in the cell. Better results were obtained with a continuous flow tube with 1 cm diameter side arms carrying the electron beam: this reduced the beam current (maximum reached was 1.6 μA) and the luminescence was weak. Light emitted at right angles to both flow and beam was analysed with a Bausch and Lomb $f/4$ grating monochromator (33-86-02)

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* Present address: I.C.I. Fibres Ltd., Middlesbrough, Yorks.

** Request reprints etc. should be sent to Dr. B. BROCKLEHURST, Chemistry Department, The University, Sheffield S3 7HF, U.K.