

THERMAL ISOMERIZATION OF DIMETHYL MALEATE

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EARLY experimental work on the kinetics of thermal cis - trans isomerizations in the gas phase indicated that these reactions were typical unimolecular processes¹. For three of these reactions, however, the temperature dependence of the rate coefficients was reported to be anomalously small. Thus for the isomerizations of cis-2-butene², dimethyl maleate³ and dimethyl citraconate⁴ respectively, frequency factors of $10^{0.5}$, $10^{5.1}$ and 10^5 sec⁻¹ were found instead of the $10^{13\pm3}$ sec⁻¹ frequency factor predicted by the usual theories of unimolecular reactions and found experimentally for all other gas phase isomerizations. Theoretical speculations⁵ ascribed the anomalous frequency factors of the second and third reactions to a reaction path involving a triplet state intermediate, and calculations were adduced to support the proposition. There were good reasons for skepticism, however, based on the findings that the high pressure limit in these reactions was reached at abnormally high pressures and that there was evidence for side reactions. Recent reinvestigations⁶ of the isomerization of cis-2-butene showed that the anomalous result of the early work was

¹A. F. Trotman-Dickenson, Gas Kinetics, Butterworths, London, 1955, Sections 2.3 and 3.3; S. W. Benson, The Foundations of Chemical Kinetics, McGraw-Hill, New York, 1960, Chapter XI.

²G. B. Kistiakowsky and W. R. Smith, J. Am. Chem. Soc. 58, 766, (1936).

³a, G. B. Kistiakowsky and M. Nelles, Z. physik. Chem. Bodenstein Festband, 369 (1931); b, M. Nelles and G. B. Kistiakowsky, J. Am. Chem. Soc. 54, 2208 (1932); c, B. Tamamushi and H. Akiyama, Z. Elektrochem. 45, 72 (1939).

⁴G. B. Kistiakowsky and W. R. Smith, J. Am. Chem. Soc. 56, 638 (1934).

⁵J. L. Magee, W. Shand and H. Eyring, J. Am. Chem. Soc. 63, 677 (1941).

⁶W. F. Anderson, J. A. Bell, J. M. Diamond and K. R. Wilson, J. Am. Chem. Soc. 80, 2384 (1958); B. S. Rabinovitch and K. W. Michel, ibid. 81, 5065 (1959); R. B. Cundall and T. F. Palmer, Trans. Farad. Soc. 57, 1956, 2226 (1961).

indeed due entirely to experimental errors, primarily in the analytical technique, and to the presence of side reactions. It was concluded that this is in fact a typical unimolecular reaction.

We have undertaken a number of experiments on the isomerization of dimethyl maleate to determine whether the anomalous early results on the kinetics of this reaction were likewise due to limitations of the analytical technique (mixed freezing points) available to the early workers. The extent of conversion to trans isomer in our experiments was held as low as possible in order to avoid erroneous results due to back reaction, product decomposition or autocatalysis. The capabilities of the vapor-chromatographic analytical technique employed were such that 1-2% trans ester could be determined with satisfactory accuracy.

The limit of experimental pressures in our experiments, which was determined by the dimethyl maleate vapor pressure in low temperature experiments and by the strength of the reaction vessels at high temperature, is substantially lower than the apparent pressure range for first-order reaction found by Nelles and Kistiakowsky^{7b}. It was thus known in advance that it would be necessary to extrapolate experimental first-order rate constants to infinite pressure. To obtain the most accurate final result for activation energy and frequency factor in a given number of experiments it was decided that the measurements would be made at two temperatures only, and that the experiments at each temperature should be distributed over the available pressure range so as to provide accurate extrapolations. The lower temperature (228.2°C) was then prescribed by a desire to complete the experiments in a reasonable (circa 12 hours) length of time. The upper temperature (301.6°C) was prescribed by the desire to remain below temperatures where the previous workers found serious autocatalytic and pyrolytic effects. The shortest reaction times at the higher temperature were 10 minutes.

The ester was prepared by conventional esterification of maleic anhydride and finally purified by painstaking fractional distillation under vacuum. VPC analysis showed that the concentrations of fumaric ester and other impurities were less than .05%. The reaction vessels were Pyrex⁷

⁷Nelles and Kistiakowsky showed by packed-vessel experiments that the isomerization was unaffected by Pyrex surfaces.

bulbs of about 30 cc. volume. They were baked at high vacuum on a mercury-pumped system before sample introduction. Samples were injected with a micro-syringe using a procedure that minimized exposure to atmospheric moisture. The bulbs were reevacuated, the dimethyl maleate being frozen over liquid nitrogen during the later stages of pumpdown, and sealed. The samples were brought to reaction temperature in a vigorously stirred, electronically regulated molten salt bath. After the reaction was terminated, by rapid cooling with a blower, the products were dissolved carefully in 1 ml. of anhydrous ether and separated totally from one another on a 60 cm. column of polyethylene glycol and silver nitrate on Chromosorb P at 100°C⁸. The extent of reaction was calculated from the relative peak areas for maleic and fumaric ester, and the pressure from weight of ester as determined by difference weighing and bulb volume as determined by titration.

The data from 8 experiments at 228.2°C, experimental pressures from 90 to 910 mm Hg, and 15 experiments at 301.6°C, experimental pressures from 110 to 2460 mm Hg, were processed on a digital computer. A least squares regression of the inverse first-order rate coefficient plotted against inverse pressure was carried out at each temperature, and the resulting rate coefficients at infinite pressure substituted into the Arrhenius law. The result, in inverse seconds units, is

$$k = 10^{9.2 \pm .8} \exp \frac{-35,500 \pm 2,100 \text{ cal}}{RT}$$

The indicated errors are standard deviations calculated from the least squares intercept variations with the usual propagation of errors formula. These values for the parameters of the Arrhenius law are lower than theoretical expectations for a normal unimolecular reaction, but do not differ sensibly from experimental findings for other unimolecular reactions. We conclude, therefore, that the anomalous frequency factors found by previous workers were due to inadequacies in their analytical method and by additional reactions taking place at the higher temperatures and higher conversions studied by them. We conclude further that there is no ground to suppose that this reaction proceeds via a triplet state intermediate, and

⁸E. Bayer, Gas Chromatography, Elsevier, Amsterdam, 1961, p. 113.

propose that there is no strong evidence for any triplet cis - trans isomerization, since the only remaining anomalous results⁴ are complicated by extensive side reaction.

The pressure dependence of the first-order rate coefficient for this reaction continues to be puzzling. The high pressure limit should be reached at a small fraction of a millimeter pressure, but the experimental result, here as in the earlier work, seems to be that there is pressure dependence up to several atmospheres. An interpretation advanced by the earlier workers was that only the rotational motion of the ester groups around the double bond could contribute to the reaction coordinate for isomerization. This interpretation accounts for the observed pressure dependence, but makes calculated values for the lifetime of activated molecules seem unreasonably long^{3b,1} in addition to running counter to expectations for energy transfer in activated molecules.

If this is in fact a unimolecular reaction, then it is a very interesting one. We could find no evidence that it is a complex reaction under the conditions studied, for no side products at concentrations greater than .05% of the dimethyl maleate concentration could be observed in our analyses⁹. It is possible, however, that this reaction, unlike other cis - trans isomerizations, may proceed to some extent by a bimolecular path. The evidence from the early work indicating an approach to a constant first order rate coefficient at 4060 mm^{3b} is not convincing in view of the large extent of decomposition observed. We are designing equipment to enable experiments using low concentrations of ester in about 20 atmospheres of argon to be carried out, in order to see whether a strict first order reaction can be observed.

⁹Occasional very small peaks (.05 x fumarate peak), whose retention times were the same as for methyl crotonate, the decarboxylation product of dimethyl fumarate, appeared in the products of some high temperature runs.