

In an octahedral complex of the composition $\text{Ma}_4\text{B}_2^{+n}$, the *trans* isomer has no net dipole moment while the *cis* isomer does. It seems reasonable for the polar ion to be more strongly held in the resin phase than the non-polar ion of the same composition and charge. Since the nitro group is one of the most polar groups, the system studied here may prove to be the one in which the separation of isomers by this method is most easily accomplished.

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THE ISOMERIZATION OF CYCLOPROPANE—A QUASI-UNIMOLECULAR REACTION

Sir:

In 1942 Pease¹ concluded that with the possible exception of the thermal isomerization of cyclopropane investigated by Chambers and Kistiakowsky,² there was no case of quasi-unimolecular reaction known, which provided unequivocal confirmation of the theory of unimolecular reactions proposed by Lindemann, Hinshelwood, Rice, Ramsperger, Kassel³ and others. Later Corner and Pease⁴ reinvestigated the isomerization of cyclopropane to propylene and concluded that as the addition of unreactive gases had little effect, the fall-off of the apparent first-order rate constant was more reasonably explained by a complex reaction mechanism than by an energy transfer process.

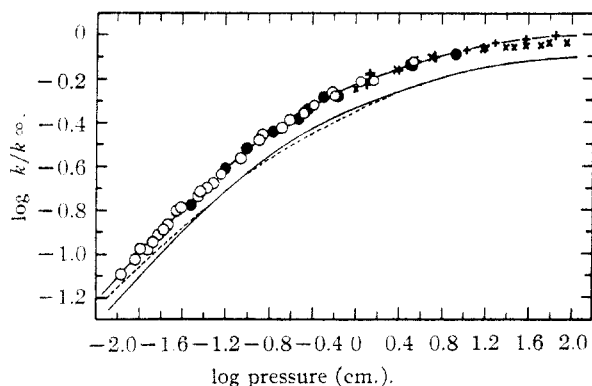


Fig. 1.

There now appear to be two well-established cases of the falling-off of unimolecular rate constants in the decomposition of nitrogen pentoxide⁵ and nitrous oxide.⁶ We have reinvestigated the isomerization of cyclopropane at 492° in a 2-l. Pyrex reaction vessel extending the measurements below the 10 mm. pressure limit of previous workers down to 0.1 mm. The reaction was followed by the

(1) R. N. Pease, "Equilibrium and Kinetics of Gas Reactions," Princeton, N. J., 1942, p. 147.

(2) T. S. Chambers and G. B. Kistiakowsky, *THIS JOURNAL*, **56**, 399 (1934).

(3) L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, N. Y., 1932, p. 93.

(4) E. S. Corner and R. N. Pease, *THIS JOURNAL*, **67**, 2067 (1945).

(5) H. S. Johnston and R. L. Perrine, *ibid.*, **73**, 4782 (1951).

(6) H. S. Johnston, *J. Chem. Phys.*, **19**, 663 (1951).

analysis of the cyclopropane-propylene mixture for olefin content on a Blacet-Leighton⁷ apparatus using a mercuric acetate bead.⁸ There is good evidence that no side-reactions occurred for in an aged reaction vessel no condensation took place and no products non-condensable in liquid nitrogen were formed. Our results are shown together with those of other workers in Fig. 1. The theoretical curve, following Chambers and Kistiakowsky,² is calculated from Kassel's³ equation using a collision diameter of 3.9 Å, 13 oscillators and a value of k_∞ , the rate at infinite pressure, given by

$$\log k_\infty = 15.17 - \frac{65,000}{2.3RT}$$

Furthermore we have investigated the effect of added hydrogen on the rate constant at low cyclopropane pressures. The hydrogen causes a marked increase in the rate constant and is about one-fifth as efficient as cyclopropane or propylene in restoring the rate constant. The comparatively low efficiency of hydrogen is evidently the reason why Corner and Pease could find no effect which in their case would have been 4%, for this is the order of their experimental error. Accordingly it seems that this reaction is a clear cut case of the falling-off of the rate of a unimolecular gas reaction with pressure.

We are now investigating the effect of the addition of a number of non-reacting gases to the system and hope to publish the results in detail when a full survey has been completed.

(7) F. E. Blacet and P. A. Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931).

(8) R. Pyke, A. Cahn and D. J. LeRoy, *Anal. Chem.*, **19**, 65 (1947).

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EFFECT OF PURINES ON A SUCCINYLSULFATHIAZOLE (SST)-INDUCED DEFICIENCY IN MICE

Sir:

The addition of succinylsulfathiazole (SST) to a purified diet having a low fat content was reported to cause a retardation of growth in weanling mice.¹ This effect on growth was prevented if such materials as fat, a defatted cottonseed meal, or rolled oats were added to the basal diet. Whereas whole liver was found to be without effect it has since been found that a water extracted liver residue is also effective. It was tentatively concluded in this earlier report that fat *per se* is an essential nutrient for animal growth. It was further suggested that in the absence of adequate quantities of dietary fat a factor, or factors, synthesized by SST-susceptible intestinal microorganisms is essential for fat synthesis by the animal. This factor, or factors, was postulated to be present in those fat-free natural materials that are capable of preventing the SST-induced growth retardation.

(1) D. K. Bosshardt, W. J. Paul, R. H. Barnes and J. W. Huff, *Proc. Soc. Exptl. Biol. Med.*, **75**, 722 (1950).