Some Reactions of cyclo*Propane and a Comparison with the Lower Olefins. Part I. Introduction, and Reaction with Strong Acids.*

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The reaction of *cyclo*propane with moderately concentrated solutions of strong acids is about five times as fast as that of propene, but the kinetics are very similar for both gases. The rate is proportional to $[C_3H_6][\text{acid}]^n$, where n is large (6—10) with aqueous perchloric or sulphuric acids but lower (2·5—3·5) with sulphuric acid dissolved in acetic acid. The products of the absorption of *cyclo*propane in the three acid solutions have been investigated. A reaction mechanism is suggested, the first step being addition of a proton to the hydrocarbon.

It has long been known that the chemical properties of *cyclo*propane are more similar to those of the lower olefins, ethylene and propene, than to those of a higher member, such as *cyclo*pentane, of the *cyclo*paraffin series (see Walsh, *Trans. Faraday Soc.*, 1949, **45**, 179, for discussion). Determinations of certain physical properties, *e.g.*, spectra and dipole moments, of *cyclo*propane derivatives have supported the view that the ring has some double-bond character (but see recent work by Eastman and Selover, *J. Amer. Chem. Soc.*, 1954, **76**, 4115, 4118), and Walsh (*loc. cit.*) has suggested that the carbon atoms in *cyclo*propane are in a state of trigonal hybridisation. However, the actual structure has been the subject of considerable controversy and so it was felt that further work on certain reactions of *cyclo*propane would yield results of interest.

The fact that both the lower olefins and *cyclo*propane are absorbed rapidly by concentrated solutions of strong acids to give esters has been known for a considerable time and is the basis of some methods for the analysis of these compounds. Davis and Schuler (*J. Amer. Chem. Soc.*, 1930, **52**, 721) and Rathmann (*J. Gen. Chem. U.S.S.R.*, 1937, **7**, 14) have investigated the rates of uptake by sulphuric acid solutions and the last showed that the absorption of *cyclo*propane was actually faster than that of propene, and that it was affected very markedly by the acid concentration. However, with the apparatus used, it is by no means certain that the results were not affected by the rate of physical solution of the gas in the acid, and no further deductions can be made. Hence, a more thorough study of the reactions of *cyclo*propane and propene with various acids was undertaken.

Experimental

The rate of reaction with various acids was followed by the conventional constant-pressure method. A certain volume of the acid was contained in a 50-ml. flask, immersed in a thermostat constant to $\pm 0{\cdot}1°$, and shaken about 250 times per min. The air in the flask had previously been swept out by *cyclo*propane or propene, and the rate of uptake of gas was followed by means of a gas-burette (in a thermostat) connected to the flask by wide capillary tubing and Polythene tubing. Before an experiment the flask was cleaned with concentrated nitric acid, water, alcohol, and redistilled water, and dried over a flame.

*cyclo*Propane was taken from a cylinder, passed through a solution of mercuric sulphate in 22% sulphuric acid, then water, and dried if necessary. Propene from a cylinder was washed and dried if necessary. " AnalaR " perchloric acid (72%), sulphuric acid, acetic acid, and methyl alcohol were used without further purification. Distilled water was redistilled in the presence of a little potassium permanganate in an all-glass apparatus. The potassium hydrogen sulphate and carbonate were of " AnalaR " standard.

Results.—The acids used were aqueous perchloric, aqueous sulphuric, and sulphuric in glacial acetic. Fig. 1 shows the results of two typical experiments. After a very rapid initial uptake due to physical solution of the gas, the rate of absorption (referred to hereinafter as the initial rate) remained constant for some time and then fell off. The initial rates were reproducible to about 5% with different specimens of the same concentration of any particular

acid, and were not affected by shaking speed provided this was above about 120 per min. It seems fairly certain therefore that the rate of uptake was equal to the rate of reaction.

The Table shows the effect on the initial rate of varying the pressure of the two gases. The results suggest that the order of the reaction with respect to *cyclo*propane or propene pressure is slightly greater than unity. However although it is unlikely that Boyle's law and Henry's law were accurately obeyed by either gas under the experimental conditions, it is probably true that the rate of reaction was approximately proportional to the concentration of *cyclo*propane or propene in the solution.

FIG. 1.

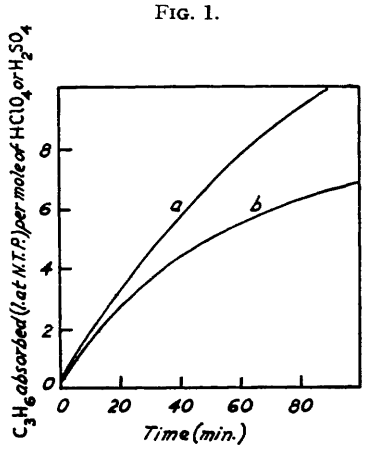


FIG. 2.

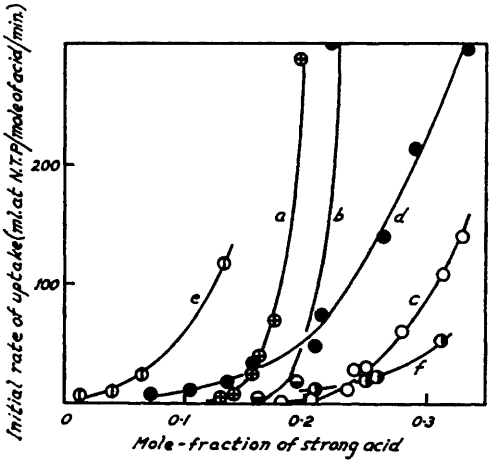


FIG. 1. *Typical* cyclo*propane uptake curves. Temp.* = 24·1°. C_3H_6 *pressure* = 760 *mm.*
(*a*) H_2SO_4 in AcOH, $N_{H_2SO_4}$ = 0·260.* (*b*) Aq. $HClO_4$, N_{HClO_4} = 0·203 (abs. × 4).

FIG. 2. *Effect of acid concentration on the initial rate of uptake† of* cyclo*propane or propene, at* 24·1°/760 *mm.*
*cyclo*Propene and (*a*) aq. $HClO_4$ (ord. × 0·1), (*b*) $HClO_4$ in aq. MeOH (ord. × 0·1), (*c*) aq. H_2SO_4 (ord. × 0·5), or (*d*) H_2SO_4 in AcOH.
Propene and (*e*) aq. H_2SO_4 (ord. × 0·1; abs. × 0·2) or (*f*) H_2SO_4 in AcOH.

Variation of the rate of uptake of cyclo*propane or propene with the pressure of the gas.* Temp. = 24·1°.

Acid	Concn.* of added acid	Gas	Initial rate † P = 600	660	760	860	920	960
Aq. $HClO_4$	0·162	*cyclo*Propane	—	3·4	3·7	3·6	—	—
Aq. H_2SO_4	0·234	,,	—	6·5	6·5	6·8	—	—
,, ...	0·240	,,	13·3	—	14·2	—	—	14·8
,, ...	0·240	Propene	8·8	—	10·0	—	10·3	—
,, ...	0·265	,,	—	23·7	23·4	26·6	—	—
H_2SO_4 in HOAc	0·105	*cyclo*Propane	—	14·7	14·5	15·1	—	—

* N = Mole-fraction. † Ml. at P mm. and 0°, per mole of acid per min.

The variation of the rate of reaction with acid concentration is shown in Fig. 2. The curves have been modified to take into account, in an approximate fashion, the variation of physical solubility of the gases with variation of concentration of acid. With aqueous perchloric or sulphuric acid the initial rate increased very rapidly as the mole-fraction of the acid was increased, the apparent orders being roughly 6·3 and 7·5 for propene and *cyclo*propane respectively in aqueous sulphuric acid and 10 for *cyclo*propane in aqueous perchloric acid. With sulphuric dissolved in acetic acid, however, the increase in rate with increasing concentration of the former was more gradual, the apparent order with respect to H_2SO_4 being about 2·6 with *cyclo*propane and 3·5 with propene. The solubility of *cyclo*propane in acetic acid was about 14 times greater than in water. Replacement of part of the water in the perchloric acid by methyl alcohol (mole-fraction ~0·4) decreased the initial rate at any particular concentration of acid, although the solubility of the *cyclo*propane was 12—15 times greater in the presence of the alcohol. However, the order with respect to acid concentration

was still very high. Separate experiments showed that there was no appreciable reaction of methyl alcohol with aqueous perchloric acid under these conditions. There was no absorption of *cyclo*propane by glacial acetic acid alone or by concentrated aqueous potassium hydrogen sulphate. Addition of powdered silica (to increase the surface) had no effect on the rate of reaction of *cyclo*propane with aqueous perchloric acid within the experimental error.

The effect of temperature on the reaction rates is shown in Fig. 3. The overall activation energies calculated from the Arrhenius plots are 16·5 and 18·0 kcal./mole for the absorption in sulphuric in acetic acid of propene and *cyclo*propane respectively, and 13·8 kcal./mole for the absorption of *cyclo*propane in aqueous perchloric acid. Each of these values includes the appropriate heat of solution of the gas in the acid.

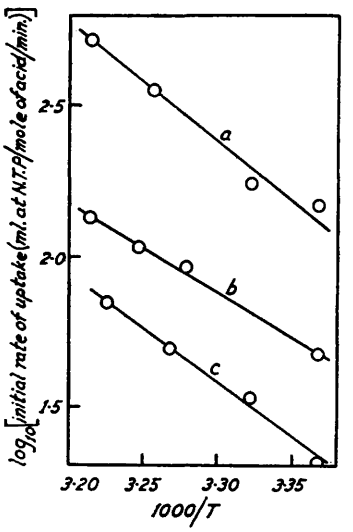


FIG. 3. *Effects of temperature on the initial rate of uptake of* cyclo*propane or propene at* 760 mm. *cyclo*Propane and (*a*) H_2SO_4 in AcOH ($N_{H_2SO_4}$ 0·260) or (*b*) aq. $HClO_4$ (N_{HClO_4} 0·203). (*c*) Propene and H_2SO_4 in AcOH ($N_{H_2SO_4}$ 0·249).

With aqueous perchloric acid, after relatively little uptake of *cyclo*propane an oily film formed on the walls of the reaction flask and when more gas was absorbed an oil separated which had a sharp smell and was almost certainly propyl perchlorate since its weight corresponded to the amount of gas taken up, within the experimental error. An oil also separated after relatively large absorption of *cyclo*propane in aqueous sulphuric acid. It was washed with a little water (the washings being added to the aqueous layer) and dried. Presumably it was di-*n*-propyl sulphate, which is only slightly soluble in water. However, although all the sulphuric acid was accounted for within the experimental error, either in the ester layer [the ester being assumed to be $(C_3H_7)_2SO_4$] or in the aqueous layer by titration with standard sodium hydroxide, about 30% of the gas taken up was not present in the form of propyl sulphate. Some propyl hydrogen sulphate was therefore probably formed. Absorption of *cyclo*propane in a solution of sulphuric in acetic acid did not lead to the formation of two layers. The whole was neutralised with solid potassium carbonate and extracted with ether, and the extract distilled. A fraction, b. p. 99°, with a smell of the lower esters of acetic acid was probably impure *n*-propyl acetate (b. p. 101·6°). The liquid residue left charred before distilling and probably contained di-*n*-propyl and/or propyl hydrogen sulphate.

The presence of the oily film, left on the surface of the flask until the next experiment, or of some of the non-soluble ester had no effect on the initial rates of uptake in the aqueous acids. The kinetics of the reaction were therefore not affected by the separation of the products.

Discussion

The results show that the kinetics of the reaction between acids and both *cyclo*propane and propene are very similar, though the actual rates are, of course, different, and it is likely that the mechanism is the same in both cases. The lack of quantitative knowledge of the entities (molecules, ions, and ion-pairs) in solutions of strong acids of moderate concentration makes interpretation difficult, but the higher orders can probably be explained by analogy with third-order esterifications. Consider a simple scheme of three reactions :

(1) $C_3H_6 + H^+ \longrightarrow C_3H_7^+$

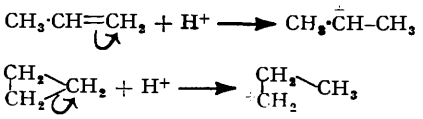
(2) $C_3H_7^+ \longrightarrow C_3H_6 + H^+$

(3) $C_3H_7^+ + HX\ (\text{acid}) \longrightarrow C_3H_7X + H^+$

If we assume that reaction (1) is slow, (2) very fast, and (3) moderately fast, the rate of uptake of gas $-d[C_3H_6]/dt = (k_1k_3/k_2)[C_3H_6][H^+][HX]$ to a first approximation. With aqueous perchloric or sulphuric acid, as the concentration of the solution was increased, the concentration of actual acid molecules would have increased rapidly from a negligible quantity in the dilute acids, and the reactions would exhibit a high apparent order. The decrease in rate of over 100-fold on replacement of a large part of the water in the aqueous

perchloric acid by methyl alcohol eliminates the possibility of any appreciable direct addition, $C_3H_6 + HX \longrightarrow C_3H_7X$, and could scarcely have been due to the decrease in dielectric constant. The protons were solvated, and it is reasonable to suppose that k_1 with H_3O^+ was very much greater than with $CH_3{\cdot}OH_2^+$. The formation of *n*-propyl acetate with sulphuric in acetic acid, together with the much lower order of reaction, supports the suggestion of reaction (3), although some addition of $C_3H_7^+$ ions to negative ions might have occurred. Dorris and Sowa (*J. Amer. Chem. Soc.*, 1938, **60**, 358) obtained a 65% yield of *n*-propyl acetate from the reaction of *cyclo*propane with acetic acid in the presence of boron trifluoride, probably by a similar mechanism. It is likely that, with aqueous sulphuric acid, propyl hydrogen sulphate was first formed, and, remaining in solution, was transformed into the dipropyl sulphate (cf. Plant and Sidgwick, *J. Soc. Chem. Ind.*, 1921, **40**, 14). Carbonium ions may be reactive towards water, but if any propyl alcohol was formed momentarily it would have reacted to give the ester under the experimental conditions, and an equilibrium $C_3H_7^+ + H_2O \rightleftharpoons C_3H_7{\cdot}OH + H^+$ would not have affected the overall result.

Whereas *cyclo*propane gives *n*-propyl esters, propene gives *iso*propyl esters (*e.g.*, Dorris and Sowa, *loc. cit.*). Thus if the first stage was the addition of a proton presumably the two reactions were



the *cyclo*propane ring acting in a similar way to the double bond. If this picture is correct then one reason why the rate of reaction of *cyclo*propane is greater than that of propene may be that the proton can attack any of three equivalent positions in the former but only one carbon atom in the latter.

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