

[CONTRIBUTION FROM THE INSTITUTE OF CHEMICAL PHYSICS, LENINGRAD, U. S. S. R.]

Analysis of Propylene and Cyclopropane in Mixtures Containing Both

BY S. Z. ROGINSKI AND F. H. RATHMANN

I. Introduction

Among the large number of monomolecular gas reactions studied up to the present time only one intramolecular transformation is known (pinene to dipentene).¹ All others are decomposition reactions of more or less complex molecules. Such transformations (isomerization) are of great theoretical interest, and especially so in the case of small molecules. Therefore it seemed of interest to study the kinetics of the isomerization of cyclopropane to propylene, one of the simplest reactions of this type. The available references in the literature for this case are contradictory and incomplete. Trautz and Winkler² believed they had here a case of a truly homogeneous reaction. Later this viewpoint was criticized on the ground that the wall reaction had not been sufficiently taken into account.³

We decided therefore to study in more detail the kinetics of this reaction. The experimental difficulties in this case are bound up with the lack of a reliable, accurate, and at the same time rapid method for the analysis of mixtures of the two gases. During the reaction the volume remains unchanged. The physical properties, and to a lesser extent the chemical properties, of the two gases are quite similar. Probably because of these difficulties the dispute as to the character of the kinetics of this reaction has remained unsolved. Hence it was necessary, before proceeding to the kinetic studies, to find a new method for the analysis of mixtures of cyclopropane and propylene.

II. Discussion

Comparative Reactions of Cyclopropane and Propylene.—The analytic methods already reported are either very inaccurate or rather tedious. As we obtained some unexpected results we believe it worth while to publish them in some detail as they may be of interest regarding the chemistry of the saturated ring compounds. The method of absorption by bromine is quite rapid but somewhat troublesome, and is moreover quite inaccurate since cyclopropane also reacts with bromine, though more slowly. The permanganate method is exceedingly inaccurate, as cyclopropane is considerably attacked by this reagent even in the cold.⁴ The immediate

(1) D. F. Smith, *THIS JOURNAL*, **49**, 43 (1927); cf. Roginski and Sapozhnikov, *J. Phys. Chem. (U. S. S. R.)*, **2**, 87 (1931).

(2) Trautz and Winkler, *J. prakt. Chem.*, **107**, 44 (1922). Cf. also G. B. Heisig, *THIS JOURNAL*, **54**, 2328 (1932).

(3) C. N. Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Clarendon Press, 1929, p. 140.

(4) *Cf. Ber.*, **21**, 1236 (1888).

catalytic conversion of propylene to polymers, thus allowing the reaction to be followed manometrically, is bound up with the difficulty of being sure the same catalyst does not affect cyclopropane.

Physical methods based on such properties as the relative specific heats, the dielectric constant, the refractive index, and the velocity of sound fail because these properties are very nearly the same for the two gases. Determination of the density of the liquefied mixtures was used by Trautz and Winkler.² This method is fairly accurate but suffers from the fact that it is tedious and requires the use of special apparatus and low temperatures as well as large amounts of the gas mixtures. Similar objections apply to methods involving the melting points.

Finding no reagent which would react with the one but not with the other gas we determined the relative reactivities of the two gases toward several reagents. This method was then used directly as a first approximation and, after correction for the reaction of the less reactive gas, for an accurate determination of the composition of the mixture. Neutral, acid and alkaline permanganate, bromine solutions, iodine solutions, bromine-iodine solutions, and various concentrations of sulfuric acid were tried. The latter method had been used for analyzing gas mixtures of the olefin series, but was found by Davis and Quiggle⁵ and by Davis and Schuler⁶ as in our case to be unsuccessful. In most cases propylene disappeared more rapidly than did cyclopropane but in the case of sulfuric acid the decided reverse of this was true. This is remarkable for it stands in direct contradiction to what one might expect. Hydrogen bromide seems to have a similar effect. Gustafson⁷ also reports the catalysis of ring breakage by acid in the case of the bromine addition reaction. Only in the case of iodine-bromide solutions were the relative rates of disappearance of the two gases sufficiently different for the method to be used analytically. The formation of the very soluble though not very stable iodine tribromide allows the reserve bromine concentration to be increased several-fold. The iodine as bromide has no effect on the rate of the bromine-cyclopropane reaction whereas it catalyzes the bromine-propylene reaction in a specific way to a very marked degree, although if the amount of bromine is kept constant, a large amount of iodine does decrease the rate, probably because the bromine *concentration* is thus greatly decreased.

III. Experimental Part

1. **Preparation of the Gas.**—Cyclopropane was prepared by the method of Erdmann⁸ from zinc dust and trimethylene bromide. It was washed with alcohol, water, and aqueous solutions of potassium permanganate. Four and even eight wash bottles of potassium permanganate were not sufficient to remove all the propylene formed

(5) Davis and Quiggle, *Ind. Eng. Chem., Anal. Ed.*, **2**, 39 (1930).

(6) Davis and Schuler, *THIS JOURNAL*, **52**, 721 (1930).

(7) Gustafson, *Compt. rend.*, **131**, 273 (1898).

(8) Erdmann, *J. prakt. Chem.*, **76**, 512 (1907).

during preparation, so it was passed through a bottle of bromine-iodine solution, then through two bottles of potassium hydroxide, and into a gas holder over strong aqueous potassium hydroxide.

Propylene was prepared by the action of phosphorus pentoxide on isopropyl alcohol, passed through two wash bottles of potassium hydroxide and into a gas holder over strong aqueous potassium hydroxide. Both gases were freed from air by freezing them out in a trap immersed in liquid air. Usually, however, the air was not removed.

2. The Absorptions.—The apparatus used was an ordinary Hempel gas absorption apparatus. The gas burets were filled with strong potassium hydroxide (or mercury). The volume of gas was measured several times during the absorption, and the time of each reading measured by a stop watch. As the gas required some time to pass through the capillary tubes between the buret and the absorption bulb, the measurement of time intervals was subject to an error of several seconds, which is quite appreciable in the more rapid absorptions. From these readings the volume of gas absorbed was obtained, and the fraction of propylene or cyclopropane absorbed computed. In the graphs this fraction is plotted against the time.

3. Absorption by Permanganate.—Both propylene and cyclopropane are attacked by neutral potassium permanganate in concentrations from 0.03 to 0.3 molar. Propylene is fairly readily absorbed but 90% absorption in 0.3 molar (nearly saturated) potassium permanganate required about half an hour and in the meantime about 10% of cyclopropane is also absorbed.

4. Absorption by Sulfuric Acid.—In a series of solutions of sulfuric acid varying in density from 1.59 to 1.83, and at temperatures from 0 to 25°, cyclopropane was *always* more readily absorbed than was propylene. The relative rates of absorption were in no case sufficiently different for any but the roughest analyses. The details will be published later.

5. Absorption by Iodine.—Both propylene and cyclopropane are slowly absorbed by aqueous iodine, iodine in KI(KI₃) or by an alkaline iodine solution. It is interesting to note that the rates of absorption for the two gases differ less than in the case of absorption by bromine although the combined action of the two causes a great difference in the two rates.

6. Absorption by Bromine and Bromine-Iodine Solutions.—Absorptions by means of bromine or bromine-iodine solutions were carried out in Hempel bulbs of 4.0 cm. diameter. The temperature was kept constant to $\pm 0.2^\circ$ by a thermostat. Five different solutions were made up as follows.

	Br ₂ , g.	I ₂ , g.	Mol. ratio Br ₂ :I ₂	Total vol., cc.
0	8.3	0.00	∞	200
1	8.3	.19	69.4	200
2	8.3	1.0	13.2	200
3	8.3	3.0	4.4	200
4	33.3	13.0	4.1	200

It is to be observed that 8.3 g. of *pure* bromine will not dissolve *completely* in 200 cc. of pure aqueous solution. The addition of iodine increases the solubility of bromine. In (4) where over four times the ordinary saturation weight of bromine was used, a few drops did remain undissolved.

In graph 1 are plotted the curves for the absorption at 15°. P_n and C_n refer to propylene and cyclopropane, respectively. The subscripts 0, 1, 2, 3 and 4 refer to the solutions described above. Curve P_0 for bromine alone is less steep than P_1 . Addition of more iodine however gives a lower

rate again as shown by P_2 . P_3 with still more iodine is nearly the same as P_0 . By keeping almost the same ratio as in (3) but increasing the concentration four times, the rate is greatly increased as shown by P_4 . On the

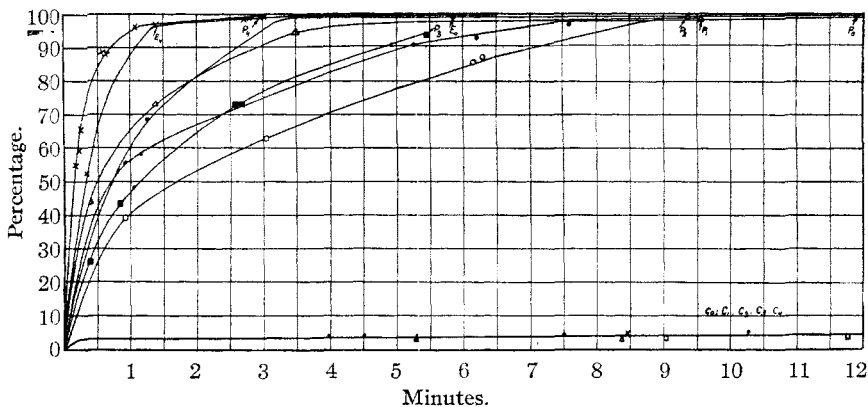


Fig. 1.—Absorption of cyclopropane (C), propylene (P), and ethylene (E) by aqueous bromine and bromine-iodine solutions: ●, solution 0; △, solution 1; ○, solution 2; ■, solution 3; ×, solution 4.

other hand, points for the curves C_0 , C_1 , C_2 , C_3 and C_4 all fall almost on the same line. Other points on the C_n curves up to 65% absorption were taken but fall outside the limits of the graph. E_0 and E_4 are some curves for ethylene absorption. Solutions of bromine alone absorb most readily at 15° and least at 0° , the solution 4 absorbs most readily at 25° and least at 0° , while solutions 1, 2 and 3 show intermediate behavior. Since the relative rates are about the same and the differences of rate small, this is not important from an analytical standpoint.

7. Absorption of Mixtures.—Graph 2 shows that in the case of propylene-air mixtures using the bromine-iodine solution number 4, the volume of gas decreases to the volume of air alone in from three to five minutes. Graph 3 shows that in the case of propylene-cyclopropane mixtures the volume quickly decreases to that of cyclopropane alone and then decreases only very slowly. Taking

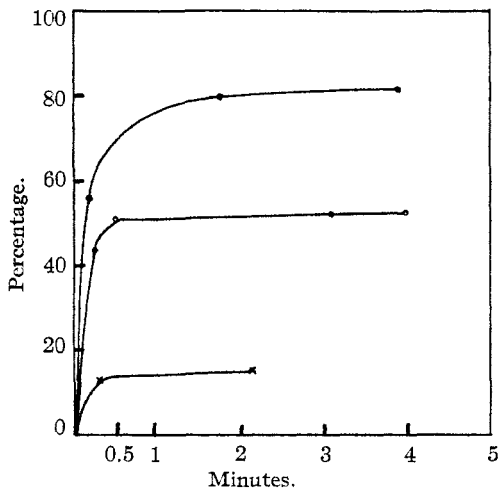


Fig. 2.—Absorption of propylene-air mixtures by solution 4.

the readings after two or after three minutes we obtain the correct result as shown in Table I.

Propylene calcd. from vol. used, %	11.6	20.7	32.7	47.0	60.0
Propylene read from graph after two minutes, %	11.9	22.2	33.0	44.7	60.5
After three minutes	12.4	..	33.5	45.5	61.2

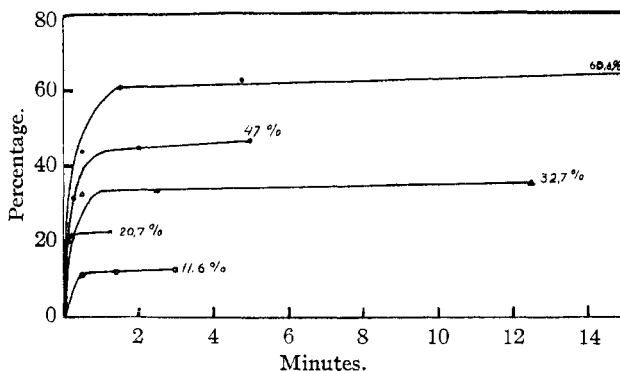


Fig. 3.—Absorption of propylene-cyclopropane mixtures by solution 4.

IV. Isomerization of Cyclopropane to Propylene

A few rough measurements were made on the isomerization of cyclopropane to propylene. At 600–650° the thermal isomerization was thoroughly studied by Trautz and Winkler.² Our measurements also showed that the conversion of the ring to the unsaturated system is slow though practically complete.

At 310, 400 and 450° the conversion in the presence of platinized asbestos is slow. In a tube of 0.9 cm. diameter and 25 cm. length, filled with old platinized asbestos, the fractions of cyclopropane converted to propylene are

Temp., °C.	Time	Vol. of gas passed through, cc.	Conversion, %
310 ± 10°	3 hrs.	ca. 100	46
310 ± 10°	3.5 hrs.	ca. 100	58
400 ± 10°	45 min.	ca. 100	44
400 ± 10°	1 hr.	ca. 100	70

while Tanatar found that at 100° after 120 hours only about 20% conversion took place in a static system.

V. Summary

1. Cyclopropane is more reactive toward sulfuric acid than is propylene.
2. Mixtures of the two gases can be conveniently, quickly and fairly accurately analyzed by means of aqueous iodine-bromine solutions. The same solution is the best means for removing traces of propylene from cyclopropane.

3. The new analytic method has been applied to some preliminary studies of isomerization transformation of cyclopropane to propylene.

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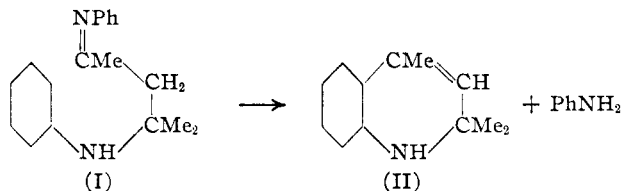
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The Alleged Formation of Aliphatic Keto-Anils¹

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The constitution of the keto-anils, $\text{ArN} = \text{CAlk}_2$, described by Knoevenagel² was discussed by Short and Watt,³ who demonstrated the presence of an NH group. Knoevenagel prepared and analyzed eight anils and twenty-five derivatives and the authors adopted his formulas, which were apparently confirmed by the analysis of a benzyl derivative which, however, could not be recrystallized owing to its excessive solubility.⁴ Reddelien and Thurm² have recently shown that acetoneanil possesses the formula $\text{C}_{12}\text{H}_{15}\text{N}$ instead of $\text{C}_9\text{H}_{11}\text{N}$ and that its properties are entirely different from those of typical anils. Its properties are in fact consistent with its formulation as a dihydroquinoline derivative (II) derived from a dimeric form (I) of the true acetoneanil by loss of aniline.⁵



In agreement with the conclusions of Reddelien and Thurm we find that (1) the formula of "acetoneanil" is $\text{C}_{12}\text{H}_{15}\text{N}$ and this is confirmed by the analysis of its acetyl and benzoyl derivatives, (2) the acetyl derivative readily loses the acetyl group on hydrolysis but the "anil" itself does not suffer hydrolysis, (3) reduction of acetoneanil with sodium and alcohol yields the base $\text{C}_{12}\text{H}_{17}\text{N}$ described by Knoevenagel but this cannot be a tetramethylindoline since no trace of aniline is formed as by-product, (4) a considerably higher yield of "acetoneanil" is obtained by increasing the

(1) This communication takes the place of a more extended manuscript which was submitted for publication before the appearance of the paper by Reddelien and Thurm which covers the same experimental ground.

(2) For a complete list of references see a memoir by Reddelien and Thurm, *Ber.*, **65**, 1521 (1932).

(3) Short and Watt, *J. Chem. Soc.*, 2293 (1930).

(4) Reëxamination of the original specimen conducted in collaboration with Mr. J. S. Watt has shown the compound is in reality an impure specimen of "acetoneanil." The picrolonate separated from alcohol in rectangular yellow prisms m. p. 173° dec. *Anal.* Calcd. for $\text{C}_{22}\text{H}_{25}\text{O}_5\text{N}$: C, 60.40; H, 5.26; N, 16.02. Found: C, 60.43, 60.22; H, 5.20, 5.34; N, 16.09.

(5) See also von Auwers, *Ber.*, **66**, 59 (1933).