Anal. Calcd. for $(C_4H_6O_2)_{18}$: C, 55.81; H, 7.02; mol. wt., 1549; sapn. equiv., 86.09. Found: C, 55.95; H, 6.99; mol. wt., 1536 (Rast); sapn. equiv., 88.14.

When a larger sample of the above dimethylpolyglycolid was saponified by refluxing it with 0.1 *N* alcoholic potassium hydroxide, a solid acid was recovered which was recrystallized from chloroform, yield 80%, m.p. 79.5°; mixed m.p. with an authentic sample of α-hydroxyisobutyric acid gave no depression; neut. equiv. 104.8, calcd. for α-hydroxyisobutyric acid 104.1.

Lucidol Polymer.[2b]—This was recrystallized several times from ethanol and the crystals subjected to a high vacuum for 48 hr. at the temp. of boiling acetone, m.p. 148–149°. The infrared spectrum of this solid (10% in CHCl₃) was identical with that of our dimethylpolyglycolid, m.p. 170–171°.

Anal. Calcd. for $(C_4H_6O_2)_{10}$: C, 55.81; H, 7.02; mol. wt., 861; sapn. equiv. 86.09. Found: C, 55.60; H, 7.37; mol. wt., 890 (Rast); sapn. equiv., 88.87.

Saponification of this solid with alcoholic potassium hydroxide gave about 80% α-hydroxyisobutyric acid.

Decomposition of *t*-Butylperoxy Isobutyrate in Boiling Water.—When 1 g. of pure *t*-butylperoxy isobutyrate was allowed to decompose under reflux of 50 cc. of water, a white solid appeared floating on the surface of the water after 3 hr. of heating. Refluxing was continued for 24 hr., then the

mixture cooled, the solid separated and recrystallized from ethanol, m.p. 148–149°; mixed m.p. with the purified solid obtained from Lucidol gave no depression.

The filtrate was treated with sodium bicarbonate and extracted with ether. Acetone was identified in the ether layer *via* its 2,4-dinitrophenylhydrazone. The sodium bicarbonate layer was acidified with hydrochloric acid and extracted with chloroform from which was obtained α-hydroxyisobutyric acid, m.p. 79–80°; mixed m.p. with an authentic sample showed no depression.

Dimethyldiglycolid (I).—This diglycolid was synthesized in accordance with the method of Blaise and Bagard[6] and purified by fractional distillation under reduced pressure and recrystallization from pentane, m.p. 80–81°, mixed m.p. with α-hydroxyisobutyric acid 60–62°; sapn. equiv. 86.12, calcd. for the diglycolid (I) 86.09; mol. wt. 167 (cryoscopic in benzene), calcd. for (I) 172.18. The infrared spectrum (10% in CHCl₃) of this diglycolid is compared (*vide infra*) with the infrared spectra of the polyglycolids.

Stereochemistry of Radical Processes. Stereospecific *trans* Addition of HBr to Propyne

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Under illumination propyne and HBr react rapidly in the liquid phase (−78 to −60°) in a stereospecific *trans* radical process, producing *cis*-1-bromo-1-propene. Gas phase reactions are markedly accelerated by light and oxygen. The stereochemistry of the gas phase addition is obscured by the rapid equilibration of the 1-bromo-1-propenes. In the gas phase, at equilibrium, the *cis* to *trans* ratio is 4.14.

Introduction

With rare exceptions radical–olefin addition reactions have been reported to be non-stereospecific.[1] Walling, Kharasch and Mayo[2] described a noteworthy exception in the addition of HBr to 2-butyne. The reaction was carried to completion with excess HBr and the product was *d,l*-2,3-dibromobutane contaminated by a small amount of 2,2-dibromobutane (from competing ionic addition). The *d,l*-2,3-dibromobutane could have resulted from two successive *trans* (or *cis*) additions.[3] However, reflecting the then current concepts of configurational instability of free radicals the authors dismissed the possibility that the successive steps were stereospecific.[4] Subsequent reports by Epstein[5] and Goering and Larsen[6] indicated that *cis*-2-bromo-2-butene yields *meso*-2,3-dibromobutane and *trans*-2-bromo-2-butene yields *d,l*-2,3-dibromobutane. Since the latter are *trans* additions, by inference the addition of HBr to 2-butyne produces *trans*-2-bromo-2-butene by *trans* addition of HBr to the acetylenic bond.

However, it does not follow from the evidence that the observed addition to an acetylene was exclusively a radical process, for an ionic reaction could equally well account for the conversion of 2-butyne to *trans*-2-bromo-2-butene, this followed by a radical sequence for addition of the second HBr. Since the interpretation of the stereochemistry of the first step in the HBr–acetylene reaction stems from circumstantial evidence, the radical HBr–propyne reaction was re-examined. Propyne was chosen because *trans* addition would involve the most sterically compressed of the radical pairs,

$$\underset{\overset{\diagdown}{}}{CH_3} \quad \underset{\overset{\diagup}{}}{Br}$$
$$.C = C, \text{ thus providing a firmer base}$$
$$\underset{H}{\diagdown}$$

for a rationale of the steric course of the reaction and the stability of the intermediate radical.

There appears to be agreement in the literature that addition of HBr to terminal acetylenes in the presence of radical inhibitors and/or Lewis-type acids produces $RCBr=CH_2$ and $RCBr_2CH_3$.[7-12]

(1) P. S. Skell, R. C. Woodworth and J. H. McNamara, THIS JOURNAL, **79**, 1253 (1957).

(2) C. Walling, M. S. Kharasch and F. R. Mayo, *ibid.*, **61**, 1711 (1939).

(3) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 295.

(4) Reference 2, footnote 4; see also ref. 8, footnote 4.

(5) M. Epstein, University of Syracuse Thesis, 1951.

(6) H. L. Goering and D. W. Larsen, THIS JOURNAL, **79**, 2653 (1957).

(7) M. Réboul, *Ann. chim. phys.*, [5] **14**, 465 (1878).

(8) M. S. Kharasch, J. G. McNab and M. C. McNab, THIS JOURNAL, **57**, 2463 (1935).

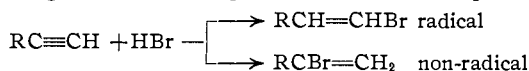(9) P. L. Harris and J. C. Smith, *J. Chem. Soc.*, 1572 (1935).

(10) C. A. Young, R. R. Vogt and J. A. Nieuwland, THIS JOURNAL, **58**, 1806 (1936).

(11) M. S. Kharasch, H. Engelmann and F. R. Mayo, *J. Org. Chem.*, **2**, 288 (1937).

(12) M. S. Kharasch, S. C. Kleiger and F. R. Mayo, *ibid.*, **4**, 430 (1939).

Addition of HBr to terminal acetylenes in the presence of peroxides has been reported as follows. (A) Propyne yields 1,2-dibromopropane, preliminary experiments indicating difficulty in stopping at the 1-bromo-1-propene state.[8] (B) Undecynoic acid yields 11-bromo-10-undecenoic acid, m.p. 18.6°.[9] Since from alkaline dehydrobromination of 10,11-dibromoundecanoic acid a small amount of 11-bromo-10-undecenoic acid, m.p. 41°, had been reported,[13] one might ascribe *trans* configuration to this acid and *cis* configuration to the 18.6° acid. Thus *trans* addition of HBr might be inferred. (C) 1-Butyne yields 1-bromo-1-butene and 1,2-dibromobutane.[10]

Thus orientation in the first step of addition of HBr to terminal acetylenes is a sufficient criterion for distinguishing radical and non-radical mechanisms. A two-step addition to terminal acetylenes yielding the dibromoparaffins does not provide

$$\text{RC}\!\!\equiv\!\!\text{CH} + \text{HBr} \longrightarrow \begin{cases} \longrightarrow \text{RCH}\!\!=\!\!\text{CHBr} \quad \text{radical} \\ \longrightarrow \text{RCBr}\!\!=\!\!\text{CH}_2 \quad \text{non-radical} \end{cases}$$

information for characterization of the first step, since both RCH=CHBr and RCBr=CH₂ yield RCHBrCH₂Br as the predominant product[11,12] under radical-addition conditions.

Results

The *cis-* and *trans-*1-bromo-1-propenes were distinguished through their infrared spectra[14] and retention times in vapor phase chromatographic (v.p.c.) separations.

Liquid phase reactions were carried out in a vacuum line using approximately equimolar amounts of propyne and HBr. The reactants were irradiated with an ultraviolet source through Pyrex glass walls at temperatures between −78 to −60°. Since the periods of illumination were short the radical chain length probably was large. The only products formed in significant amounts were *cis-*1-bromo-1-propene and 15–20% 1,2-dibromopropane. The isomeric substances *trans-*1-bromo-1-propene, 2-bromopropene and allyl bromide could not be detected, thus placing an upper limit of approximately 1% conversion to these products.

Gas Phase Reactions.—Conditions for gas phase reactions were chosen to avoid condensation of the bromopropenes and thus minimize reactions in a condensed phase. When proceeding to high conversions in the presence of excess HBr, a liquid phase of dibromide separated during the later stages of the reaction, a condition which was usually avoided.

The rate of the gas phase reaction was extremely variable, under laboratory or ultraviolet source illumination generally showing a short inhibition period, a fast reaction to 50–70% conversion and finally a slow reaction for the remainder. Although all the details of this sequence are not rationalized at present, some of the factors are apparent and will be discussed below.

All gas phase reactions yielded ultimately as the major products an equilibrium mixture of *cis-* and *trans* - 1 - bromo - 1 - propene. Occasionally small amounts of 2-bromopropene were found, but often none could be detected, indicating this is a by-product (possibly produced on the walls which would slowly accumulate a white deposit of mercury compounds).

To demonstrate that an equilibrium mixture of 1-bromo-1-propenes was being produced, a reaction mixture of 100 mm. propyne, 100 mm. HBr and 5 mm. O₂ was carried to 84% conversion by irradiation with an ultraviolet source for 30 minutes. The infrared spectrum of the reaction mixture in gas phase showed a ratio of optical densities at 14.55 μ (*cis*) and 13.85 μ (*trans*) of 7.23. To 51.0 mm. propyne and 40.0 mm. HBr, 49.0 mm. of *cis-*1-bromo-1-propene was added and the reaction was carried to 87.5% conversion of HBr by irradiation for 8 minutes. The corresponding ratio of optical densities was 7.20, thus demonstrating that the added isomer was isomerized under the reaction conditions for the propyne–HBr reaction.

In an independent experiment the 1-bromopropenes were brought to equilibrium in the gas phase with a trace of iodine and illumination. At equilibrium the ratio of optical densities was 7.09. Determination of the extinction coefficients on pure samples made it possible to calculate a value of 4.14 for the gas phase equilibrium constant at 24–26°.

$$[cis]/[trans] = 4.14$$

V.p.c. analysis of the same mixture yielded a ratio of peak heights for the two isomers of 4.19 (ratio of areas 4.02). This value can be compared with the value of 2.12 reported for the neat liquids.[14] The equilibrium constants for the dibromoethylenes (*cis/trans*) has been reported 1.04 in gas phase at 50°,[15,16] 1.28 in CCl₄ solution at 50°[16] and 1.70 for the neat liquids at room temperature.[17]

The rapid isomerization of the 1-bromo-1-propene products under the reaction conditions for gas phase addition of HBr to propyne makes it impossible to draw from the above data any inference about the stereochemistry of the primary processes. Considerable effort was expended to circumvent the difficulties resulting from isomerization of the primary product, mainly in the direction of observing the product compositions in the early stages of the reaction. It was hoped that immediately after the induction period only one isomer would appear initially and the other could be observed after an appreciable amount of the first had been produced. Two techniques were used. The first employed the cycling performance of the Perkin–Elmer model 21 infrared spectrophotometer, cycling at maximum speed between 13.70 and 14.60 μ to observe the absorption maxima at 13.85 (*trans*) and 14.55 μ (*cis*). The ratio of optical densities at these wave lengths was 7.6 and 7.20 at 59% (0.9 min.) and 90% (3.1 min.) conversions, respectively, indicating an equilibrium mixture of the 1-bromo-1-propenes. The mini-

(13) F. Krafft, *Ber.*, **29**, 2232 (1896).

(14) K. E. Harwell and L. F. Hatch, This Journal, **77**, 1682 (1955). We are indebted to Professor L. F. Hatch, The University of Texas, for sending us gas and liquid phase spectra of these isomers. Spectra of pure samples obtained in our laboratory agree in complete detail with those provided by Professor Hatch.

(15) R. M. Noyes and R. G. Dickinson, *ibid.*, **65**, 1426 (1943).

(16) H. Steinmetz and R. M. Noyes, *ibid.*, **74**, 4141 (1952).

(17) A. R. Olsen and W. Maroney, *ibid.*, **56**, 1320 (1934).

mum cycling frequency imposed by the design of the instrument was 25 seconds. To make observations at earlier stages of the reaction the second technique was developed. An auxiliary high speed time *vs.* potential recorder was operated off a potential-dividing helipot attached to the pen-drive mechanism of the spectrophotometer set at 13.85 or 14.55 μ. In this way the increase of concentration of one isomer could be followed as a function of time. By carrying out successive experiments, alternating the wave length being observed for each experiment, it was hoped that immediately following the induction period one optical density would increase precipitously and the other gradually. A number of experiments indicated both optical densities increased precipitously. Since both wave lengths could not be followed simultaneously for any one experiment a quantitative comparison of optical densities is not significant. These experiments indicated that further experimentation should go in the direction of simultaneous observations of both peaks during the 0–4 second interval. In principle the question toward which these experiments were directed can be answered by this technique, but the relatively slow response of the model 21 detection system precludes extension of the method in this direction. Alternative experimental techniques are being examined.

Initiation of the Radical Reaction.—The rate and the induction period of the gas phase propyne–HBr reaction were sensitive to changes of oxygen concentration and the level of illumination. At ordinary room level of illumination the reaction does not occur in the absence of oxygen. At the same level of illumination the addition of oxygen to a partial pressure of 10 mm. will bring the reaction 80–90% to completion in 10–15 seconds. At oxygen partial pressures in the vicinity of 0.02 mm. the reaction is extremely slow (0.2% min.) and the effect of radiation intensity is demonstrated readily by placing a 50 watt tungsten light bulb close to the reaction vessel (10%/min.). The primary products of acetone photolysis also initiated the reaction. These effects are illustrated in Fig. 1.
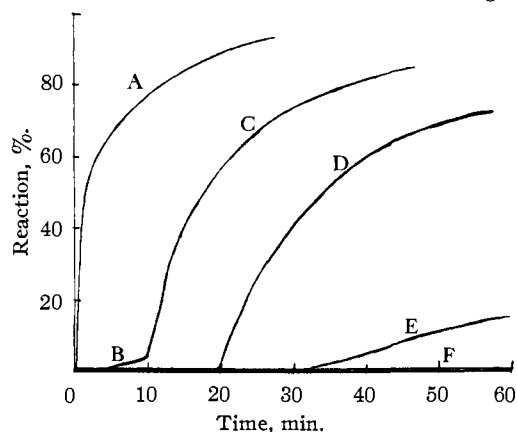

Fig. 1.—Rates of gas phase HBr–propyne reactions for 1:1 mixtures, total press. 150–200 mm.: A, 10 mm. O_2, ultraviolet light; B, 0.02 mm. O_2, ambient light; C, 0.02 mm. O_2, ultraviolet light; D, 10 mm. acetone, ultraviolet light; E, no O_2, ultraviolet light; F, no O_2, dark.

Discussion

Propyne and HBr, in both liquid and gas phase radical-initiated reaction produce 1-bromo-1-propenes as the major products. In liquid phase at -78 to $-60°$ the reaction is stereospecific and *trans*, producing *cis*-1-bromo-1-propene. The gas phase reaction is complicated by a parallel reaction which results in isomer equilibration of the initially produced 1-bromo-1-propene.
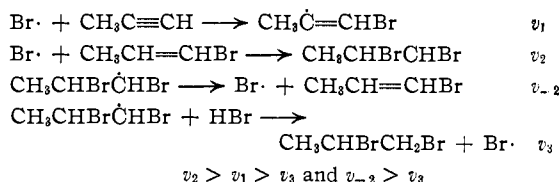

$$CH_3C\!\equiv\!CH + HBr \xrightarrow{gas} \text{equil. mixt. of 1-bromo-1-propenes}$$
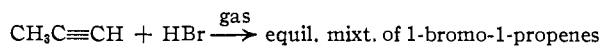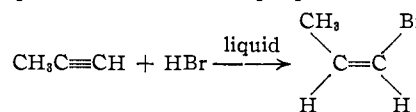
The liquid phase results can be explained by either of two distinct rationales[18]: (1) addition of a bromine atom produces a stable *cis* radical
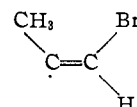
or (2) reaction occurs by addition of ·Br to a propyne–HBr complex, closely followed by transfer of the hydrogen atom, or the reaction is termolecular (propyne, HBr and ·Br). It was hoped that experiments in the gas phase would shed light on these possibilities.

Gas phase studies have not yielded a definitive conclusion because the product is rapidly isomerized under the addition reaction conditions. Some of the relative reaction velocities can be adduced from these experiments. Reaction conditions were chosen (100 mm. propyne, 100 mm. HBr) so that 100% conversion would not produce a gas saturated with bromopropenes. Thus observed condensation of liquid would be attributable to formation of dibromide. Since condensation of liquid occurred only in the later stages of the reaction, it can be concluded that propyne and the 1-bromo-1-propenes add HBr at comparable over-all velocities. This conclusion and the fact that the 1-bromo-1-propenes are isomerized in the gas phase reactions more rapidly than they are produced leads to the following order of reaction velocities under these conditions

$$Br· + CH_3C\!\equiv\!CH \longrightarrow CH_3\dot{C}\!=\!CHBr \qquad v_1$$
$$Br· + CH_3CH\!=\!CHBr \longrightarrow CH_3CHBrCHBr \qquad v_2$$
$$CH_3CHBr\dot{C}HBr \longrightarrow Br· + CH_3CH\!=\!CHBr \qquad v_{-2}$$
$$CH_3CHBr\dot{C}HBr + HBr \longrightarrow$$
$$CH_3CHBrCH_2Br + Br· \qquad v_3$$

$$v_2 > v_1 > v_3 \text{ and } v_{-2} > v_3$$

Extension of this work in the propyne and other acetylenic systems is in progress.

Experimental

Purification of Materials.—Commercial anhydrous hydrogen bromide was shaken with mercury, distilled through a $-78°$ trap and condensed at $-195°$ at 10^{-5} mm.

(18) The conclusion from spectroscopic analysis [D. A. Ramsay, *Ann. N. Y. Acad. Sci.*, **67**, 485 (1957)], that in the ground state H—Ċ=O is bent (120°) and that an electronic state lying 23 kcal. above the ground state is linear, lends considerable credence to the possibility that other vinyl radicals have structural parameters similar to the parent olefin.

Commercial propyne contained as much as 13% acetylene and a small amount of high boiling material, probably 2-butyne. Distillation at 10^{-5} mm. through a $-78°$ trap and condensation at $-111.5°$ yielded a product containing 0.5% acetylene. Since acetylene is less reactive than propyne and appears to have no effect on the course of the reaction, further purification was not deemed necessary. The vapor pressure of propyne is 21.8 mm. at $-78°$.

Dehydrohalogenation of propylene dibromide by sodium phenolate in ethanol[19,20] yielded a mixture of the isomeric bromopropenes which were not separated satisfactorily by distillation through a 36 in. × 1.5 cm. glass helices packed column, presumably a consequence of isomerization during the distillation. Vapor phase chromatographic separation on a 9-ft. column of 30% dipropylene glycol dibenzoate on 30–60 mesh firebrick at 91°[21] yielded pure samples of 2-bromopropene (44%), cis-1-bromo-1-propene (38%) and trans-1-bromo-1-propene (18%). 2-Bromo-1-propene, cis-1-bromo-1-propane and trans-1-bromo-1-propene had retention times of 9.1, 12.2 and 15 min., respectively, at a helium flow rate of 64 ml./min., i.d. of column 8 mm.

Liquid Phase Reaction of Propyne and HBr.—In a vacuum line 14.8 mmol. of propyne and 13.5 mmol. of HBr were condensed into a borosilicate glass tube at $-195°$. The reaction mixture was placed in a $-78°$ bath and then irradiated by removing the bath and placing a G. E. RS reflector sunlamp 1 inch from the tube. When the pressure increased to approximately 150 mm., the $-78°$ bath was replaced. Alternative application of the lamp and the bath was repeated at approximately 1-min. intervals over a period of 20 min., making the total time of irradiation 10 min. Unreacted starting material (4.7 mmol.) was removed to a $-198°$ bath through a $-78°$ bath which trapped the bromopropene and propylene bromide produced. The product was 70% bromopropene and 30% propylene bromide as determined by vapor phase chromatography. Gas infrared spectra and vapor phase chromatography indicated the bromopropene fraction to be cis-1-bromo-1-propene uncontaminated by trans-1-bromo-1-propene (13.85, 13.64, 10.72 μ), 2-bromopropene (11.29, 8.47, 8.58 μ) and allyl bromide (11.26, 10.18, 10.04, 8.50 μ).

Gas Phase Reactions of Propyne and HBr.—A volumetrically calibrated vacuum line was employed, the reaction being followed by pressure decrease, or change in optical density at 13.85 μ (trans) and 14.55 μ (cis), or vapor phase chromatography, frequently using two methods simultaneously. Since the conclusions from these experiments were not definitive and further work is in progress, only representative experiments will be reported.

A. No Oxygen.—Purified propyne and purified HBr were introduced into a 158-ml. reaction vessel (that had been evacuated to 10^{-6} mm.) to partial pressures of 100 mm. each. The reaction was initiated by a 200 watt tungsten filament bulb and followed by the pressure drop in the system. The reaction showed an initiation period of 80 min. followed by a slow reaction that went to 45% completion in 225 min. The only products identifiable by infrared were cis- and trans-1-bromo-1-propene.

(19) G. Chavanne, Compt. rend., **158**, 1698 (1914).

(20) L. F. Hatch and K. E. Harwell, THIS JOURNAL, **75**, 6004 (1953).

(21) This v.p.c. column was used throughout this work in either 9 or 15 ft. lengths.

B. Oxygen in the System.—To a mixture of oxygen and propyne at partial pressures of 9 mm. and 100 mm., respectively, was added HBr to a partial pressure of 77 mm. The reaction mixture was irradiated with a 200 watt tungsten filament lamp. After 30 sec. the pressure in the reaction flask had dropped to 127 mm. (77% completion). In 15 min. the reaction went to 90% completion. The only identifiable products by infrared were cis- and trans-1-bromo-1-propene.

C. Acetone in the System.—To a mixture of propyne and acetone in a 158-ml. evacuated reaction flask at partial pressures of 99 and 10 mm., respectively, was added HBr to a partial pressure of 103 mm. The reaction, initiated by a 200 watt tungsten filament lamp, had a 20-min. initiation period followed by a reaction of 5% per min. After 150 min. the reaction flask pressure had dropped to 122 mm. (90% reaction). The only identifiable products by infrared were cis- and trans-1-bromo-1-propene.

Infrared Spectra.—The following infrared spectra were obtained for the pure gases in a 10-cm. cell using NaCl optics, recording wave length in microns: **cis-1-bromo-1-propene** 3.27(w), 3.34(ms), 3.45(s), 6.10(s), 6.15(s), 6.34(w), 6.63(vw), 6.89(mw), 6.94(mw), 7.18(w), 7.25(w), 7.61(vs), 7.69(vs), 8.24(mw), 8.30(mw), 9.65–9.80(vw), 10.70(s), 10.76(s), 13.00–13.25(vw), 14.55–14.65(vs), 14.80–4.90(vs); **trans-1-bromo-1-propene** 3.25(w), 3.37(m), 3.41(s), 3.65(vw), 5.10(vw), 6.00(mw), 6.11(m), 6.80(w), 6.90(w), 7.71(mw), 7.77(mw), 8.17(vs), 10.54(vs), 10.72(vs), 13.64(vs), 13.84(ms); **2-bromo-1-propene**, 3.25(mw), 3.39(s), 3.44(m), 5.62(mw), 5.67(mw), 6.10(vs), 6.45(vw), 6.90(ms), 6.94(s), 7.10(vw), 7.20(m), 7.25(m), 7.69(vw), 7.77(vw), 8.47(vs), 8.53(vs), 8.58(vs), 9.09(mw), 9.15(mw), 10.70(w), 10.80(w), 11.23(s), 11.29(vs).

Optical Densities of the 1-Bromo-1-propenes.—Optical densities were determined on the pure gases in a 10.0-cm. infrared cell vs. a NaCl plate using NaCl optics, Perkin-Elmer model 21 infrared recording spectrophotometer.

Pressure in cell, mm.	Optical density 13.85 μ	Optical density 14.55 μ
50, cis	0.022	1.280
30, cis	.013	0.950
19, cis	.006	.670
10, cis	.002	.353
5, cis	.001	.196
50, trans	.700	.060
16, trans	.307	.015
6, trans	.120	.005

Determination of K for cis–trans Isomerization of 1-Bromo-1-propenes.—A cis–trans mixture (21.6 mm.) of 1-bromo-1-propenes was placed in a 10-cm. infrared cell along with a crystal of iodine and allowed to stand 3 days taking infrared readings twice daily until the cis–trans optical density ratio remained constant for 24 hr.; optical density ratio 7.09, $K = [cis]/[trans] = 4.14$. When the sample from the infrared cell was passed through a 15-ft. v.p.c. column packed with 30% dipropylene glycol dibenzoate on firebrick at 45 cc./min. helium flow rate at 105°, the cis- and trans-1-bromo-1-propenes were separated. The ratio of peak heights was 4.19 and the ratio of areas was 4.02.

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