

vent. For example, the conductivity of halides in sulfur dioxide,¹⁷ and the first-order reactions in sulfur dioxide^{13b,18} are explained by ionization of the halide. It might be better to remark that sulfur dioxide is a reactant forming a cation-sulfur dioxide ion¹⁹ VI and halide ion, the ion VI undergoing racemization or reaction with reagents.



One recognizes VI as the product obtained by reaction of thionyl halide with one molecule of alcohol and ionization of the remaining halogen atom from the intermediate ester VII. VI can presumably give VII by reaction with halide ion. VII can presumably give halide and sulfur dioxide with or without inversion.⁵ In the formation of VI inversion or retention may be the steric result. Thus, only after careful scrutiny of the role of the solvent, sulfur dioxide, may one hope to understand the steric results of reactions in this solvent.

(17) Hückel, "Theoretische Grundlagen der organischen Chemie," Vol. II, Akademische Verlagsgesellschaft m. b. H., Leipzig, 1931, p. 269. See, however, Hughes, Ingold and Scott, *J. Chem. Soc.*, 1271 (1937).

(18) Bergmann and Polanyi, *Naturwissenschaften*, **21**, 378 (1933).

(19) See Waters and Lowry, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1937, p. 189.

The author acknowledges with pleasure the help and advice of Dr. Linus Pauling in connection with the ideas presented in this paper and in the preparation of the manuscript.

Summary

A recalculation of the data on the solvolysis of *t*-butyl chloride in alcohol-water mixtures using fugacity rate equations of the type suggested by Olson and Halford shows that the rates and product compositions can be explained assuming that the reaction between *t*-butyl chloride and solvent involves two or more solvent molecules.

The ionic mechanism of Ingold and collaborators for the first-order solvolytic reaction of halides and the explanation of the usual steric result of these reactions on the basis of shielding of the carbonium ion by the ionizing halogen atom is rejected in favor of an interpretation which regards the solvent as a reactant.

The author agrees essentially with Hammett and co-workers on a polymolecular interpretation for solvolytic reactions of halides. The difference in steric results obtained in solvolytic reactions and in exchanges involving attack by negative ions is discussed from the standpoint of possible transition states and competition between different solvent molecules or between a solvent molecule and a negative ion in the transition state.

PASADENA, CALIF.

RECEIVED MARCH 25, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

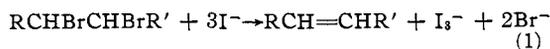
Investigations on the Stereoisomerism of Unsaturated Compounds. IV. The Identification of *cis-trans* Isomers by Rate Studies¹

BY WILLIAM G. YOUNG, DAVID PRESSMAN AND CHARLES D. CORYELL²

Introduction.—The determination of the configuration of *cis-trans* isomers of the ethylene type is a difficult problem in spite of the many modes of approach which have been suggested. None of the generally accepted³ chemical methods of identification such as ring opening or ring formation, are applicable in all cases and the most reliable physical methods require special equip-

ment which is not available in most laboratories. Consequently, it is particularly desirable to develop chemical methods of establishing the configuration of *cis-trans* isomers which can be applied easily and which will give dependable results.

A study of the rates of reaction of the stereoisomeric ethylene dibromides with potassium iodide in 99% methanol was the most promising method considered. The reaction⁴ involved is



for which the rate is first order with respect to

(1) This work was accomplished with the aid of a grant from the Board of Research of the University of California.

(2) Part of this paper was taken from the dissertation submitted by David Pressman in partial fulfillment of the requirements for the degree of Master of Arts, and was presented at the San Diego Meeting of the Pacific Division of the American Association for the Advancement of Science, June, 1938.

(3) Gilman's "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, 1938, p. 370.

(4) Dillon, *THIS JOURNAL*, **54**, 952 (1932).

both the dibromide and iodide concentrations. It has been shown in the case of two pairs of stereoisomers, fumaric and maleic acids,⁵ and *cis*- and *trans*-2-butenes,⁶ that the *meso* dibromides (from the *trans* compounds) react more rapidly than the corresponding *d,l*-dibromides (from the *cis* compounds). It is the purpose of this paper to present the experimental results obtained with the dibromides of several more pairs of geometrical stereoisomers in which two hydrogen atoms are adjacent to the double bond, and the other two groups are identical or similar. In every case the dibromide from the *trans* isomer had the larger second-order specific reaction rate constant both at 75° and 60°, and the smaller Arrhenius heat of activation.

Nomenclature.—A convenient nomenclature has been adopted for this work which emphasizes the relationship between the parent unsaturated compound and the product of normal bromine addition (*trans* addition) by naming the product as the dibromide of the parent compound. This nomenclature is especially useful in referring to dibromides of unsymmetrical stereoisomers. *cis*- and *trans*-2-pentenenes both give racemic mixtures of 2,3-dibromopentanes which are different from each other. The names *trans*- and *cis*-2-pentene dibromide clearly show this difference by referring to the structure of the parent compound.

Experimental Procedure

Measurement of Reaction Rates

Technique.—The following procedure was used to follow the rate of reaction of the various dibromides with potassium iodide: a solution containing the dibromide, approx. 0.025 molal, and potassium iodide, approx. 0.25 molal, in 99% methanol was prepared at 20°. Eight or ten 20.00-ml. aliquot portions of this solution were then sealed in test-tubes and placed in a thermostat at 75 or 60°. For any given run the temperature was constant to within 0.03°. Tubes were removed at measured intervals and quenched in ice water, broken in an acidified aqueous solution of potassium iodide, and titrated for iodine with 0.015 *N* sodium thiosulfate solution.

Due to the very slight solubility of the *trans*-stilbene dibromide in methanol, it was necessary to use acetone to make a comparison of the isomeric stilbene dibromides. The *trans*-dibromide, 0.003 *M*, liberated iodine from sodium iodide, 0.125 *M*, at an appreciable rate at room temperature and had reacted completely in eighteen hours, whereas the *cis*-dibromide under the same conditions liberated only 5% of the theoretical quantity in eighteen hours.

Calculation of the Rate Constants.—An analysis of equation (1) for the reaction first order

(5) Van Duin, *Rec. trav. chim.*, **43**, 341 (1924); **48**, 345 (1926).

(6) Dillon, Young and Lucas, *THIS JOURNAL*, **52**, 1953 (1930).

with respect to both dibromide and iodide concentrations leads to the following equation connecting initial iodide concentration *a*, initial dibromide concentration *b*, fraction ϕ of the dibromide consumed, and *t*, time in hours

$$d \log_{10} \frac{1 - 3b\phi/a}{1 - \phi} / dt = \frac{a - 3b}{2.303} k_{\text{obsd.}} \quad (2)$$

Values of $\log_{10}(1 - (3b\phi/a)/(1 - \phi))$ corresponding to the various samples of a run were plotted as ordinates against the corresponding values of time *t*, and the best straight line was drawn through the points. The slope of this line was multiplied by the value of $2.303/(a - 3b)$ for the run to give $k_{\text{obsd.}}$ This method does not give undue weight to the first analysis made, and the value of *k* is not affected by the small time necessary to bring the solution to temperature, which would lead to a small positive intercept on the abscissa axis.

As a matter of fact, the best straight lines for many runs did not pass through the origin, but formed small positive intercepts on the ordinate axis. For a given compound, the intercepts for different runs were nearly the same regardless of temperature. Figure 1 is a plot of two runs with *cis*-3-hexene dibromide at 74.90°, which are selected as representative cases showing clearly the existence of the intercept. In a few cases the

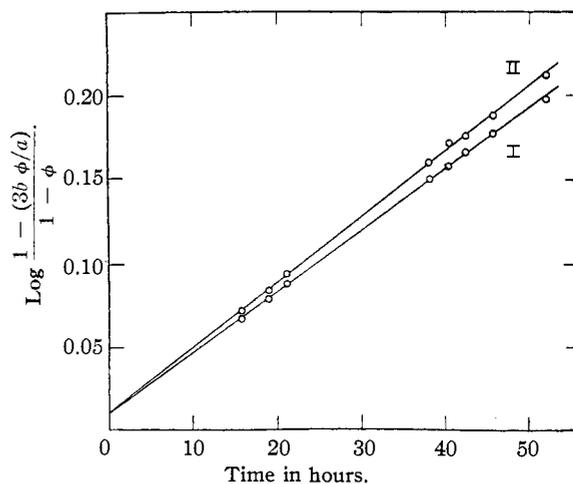


Fig. 1.—Treatment of the runs with *cis*-3-hexene dibromide at 74.90°.

value of the intercept was uncertain because the measurements had been made within a time interval which was shorter than that used in most runs. In those cases the average intercept obtained with the other runs on the same compound was assumed and the best line was drawn through the points to this assumed intercept. This pro-

TABLE I
 DATA AND CALCULATED VALUES FOR REACTION RATE CONSTANTS AND HEATS OF ACTIVATION

Parent compound	$k_{\text{obsd.}}$	Temp., °C.	KI a	Dibromide b	Intercept	k corr. ^d	k corr. KI = 0.25	Av. k	% deviation	$\frac{0}{\text{KI} = 0.25}$
<i>cis</i> -2-Butene	0.0301 ^a	74.93	0.233	0.026	0	0.0347	(0.0347) ^e	0	28.60
	.0301 ^a	74.93	.227	...	0	.0347			
	.00465 ^a	59.72	.228	...	0	.00540	(.00540) ^e	..	
<i>trans</i> -2-Butene	.0562 ^a	74.93	.222	.033	0	.0647	(.0647) ^e	..	28.00
	.00902 ^a	59.72	.229	...	0	.01046	(.01046) ^e	..	
<i>cis</i> -2-Pentene	.0528	75.00	.232	.020	0.0075	.0564	0.0570			26.50
	.0515	74.60	.272	.021	.006	.0576	.0569	.0570	0.09	
	.00915	59.49	.257	.025	(.009)	.01016	.01012			
	.00893 ^c	59.64	.177	.021	.007	.00976	.01017	.01015	.25	
<i>trans</i> -2-Pentene	.0895	75.00	.264	.021	.004	.0956	.0948			25.68
	.0849	74.60	.244	.022	(.004)	.0947	.0950	.0949	.11	
	.01611	59.49	.263	.023	.005	.01786	.01773			
	.01644 ^c	59.64	.249	.021	.003	.01793	.01794	.01784	.59	
<i>cis</i> -3-Hexene	.0472 ^c	74.90	.244	.022	.010	.05098	.05118			25.78
	.0469 ^c	74.90	.254	.020	.011	.05055	.05045	.0508	.72	
	.00843 ^c	59.41	.242	.018	.011	.009432	.00947	.00946	.11	
	.00846 ^c	59.41	.251	.022	.010	.009465	.00945			
<i>trans</i> -3-Hexene	.1332 ^c	74.90	.268	.023	.0065	.1438	.1423			24.45
	.1338 ^c	74.90	.242	.021	.005	.1444	.1451	.1437	1.00	
	.02625 ^c	59.41	.242	.022	.004	.02927	.02940			
	.02596 ^c	59.41	.244	.022	.0035	.02895	.02904	.02922	0.64	
<i>cis</i> -4-Octene	.0982 ^b	74.90	.239	.017	(.010)	.1082	.1089			25.48
	.0960 ^b	74.86	.242	.018	(.010)	.1062	.1067	.1078	1.01	
	.01862	59.49	.247	.016	(.010)	.02062	.02066			
	.01867 ^c	59.64	.242	.019	.010	.02035	.02044	.02055	0.54	
<i>trans</i> -4-Octene	.1239 ^b	75.04	.245	.016	.020	.1354	.1358	.1358	..	24.48
	.02544 ^c	59.64	.249	.017	.008	.02767	.02768			
	.02532 ^c	59.64	.250	.019	.007	.02755	.02755	.02762	0.24	
Maleic acid (<i>cis</i>)	1.014 ^b	74.90	.259	.021	(.003)	1.116	1.110			24.65
	1.033 ^b	74.90	.247	.020	.0025	1.137	1.139	1.125	1.29	
	0.1989 ^b	59.45	.238	.020	.003	0.2253	0.2269			
	.1980 ^b	59.46	.247	.022	.003	0.2241	.2245	0.2257	0.53	
Fumaric acid (<i>trans</i>)	4.195	74.55	.281	.016	-.004	4.668	4.586			20.98
	4.250	74.55	.266	.020	-.003	4.730	4.689	4.638	1.11	
	1.082	59.48	.256	.021	(.000)	1.189	1.185			
	1.048	59.48	.199	.023	.001	1.152	1.186	1.186	0.04	

^a Natural methanol, rates 7% lower than synthetic methanol I (the standard for this work). ^b Synthetic methanol II, rates 2% lower than on methanol I. ^c Synthetic methanol III, rates same as methanol I. ^d The constants have been corrected for reactivity of solvent, solvent expansion and to the temperatures 75.00 or 60.00°. ^e These calculations were made using the data reported by Dillon;⁴ correction has not been made for potassium iodide effect.

cedure gave satisfactory agreement with rate constants calculated from the runs made over longer time intervals. Table I presents the data for all runs made on the compounds to be discussed in this paper. Column 2 lists $k_{\text{obsd.}}$ while column 6 lists the intercepts found, with parentheses enclosing assumed values.

In most of the previous work in this field an integrated form of a rate equation has been used. The existence of an ordinate intercept such as was frequently found in this study would lead to calculated constants exhibiting a tendency to fall

off. This behavior has been observed by Davis and Heggie,⁷ who report that propene dibromide and 1-pentene dibromide give steadily decreasing constants. The data presented by Dillon, Young and Lucas⁶ and Dillon⁴ gave no evidence of drift in constants.

The intercepts obtained when the data are treated by our method and the drifts obtained by use of an integrated equation may be accounted for chemically on the assumption that with some compounds the reaction starts out abnormally fast

(7) Davis and Heggie, *J. Org. Chem.*, **2**, 470 (1937).

as though catalyzed but very soon becomes normal through destruction of the catalyst. In rare cases this initial liberation of iodine was observable during operations at room temperature.

Effect of Solvent on the Rate Constants.—Due to the fact that the different preparations of 99% methanol exhibited slightly different rates for the same compound, all of the rates involving methanol preparations were corrected to the value they would have exhibited in the first preparation of methanol used in this set of experiments. This was accomplished by comparing the rate constant of a standard substance, some of the original preparation of 1-butene dibromide used by Dillon, Young and Lucas,⁶ in the three different solvent preparations used in this work, as suggested by Young and Winstein.⁸ The first and third preparations gave identical rate constants while the second preparation gave a rate constant 2% smaller. Accordingly, all of the rate constants determined in solvent II were increased by 2% to afford a comparison with those determined in solvents I and II (see references to column 2, Table I).

Correction of Rate Constants to Standard Temperature.—Since different reactions were studied at slightly different temperatures in the neighborhood of 75.00 and 60.00°, all of the rate constants were corrected to correspond to those temperatures by the use of the experimentally determined temperature coefficients calculated for each compound.

Correction of Rate Constant for Solvent Expansion.—A positive error is made in volume concentrations of substances in methanol at temperatures above 20° due to the thermal expansion of the solvent between the temperature at which the tubes are made up and the temperatures at which the reaction rate is followed. Because the rate constant for a second order reaction has units reciprocal in concentration and time, there is introduced a negative error in the directly calculated values of the rate constant with increasing temperature due to the use of the 20° volume concentrations. Hence a small negative error in the apparent temperature coefficient of the rate constant is introduced. In order to correct for this error the constants at 60° were increased by 4.8% and those at 75° were increased by 6.8% in accord with the measurements⁹

(8) Young and Winstein, *THIS JOURNAL*, **58**, 102 (1936).

(9) Landolt-Börnstein, "Tabellen," Verlag von Julius Springer, Berlin, 1923, Vol. I, p. 278.

on the density of methanol at 20, 60 and 75°. The rate constants corrected for effect of solvent, temperature and alcohol expansion are listed in Table I, column 7.

Correction of Rate Constant for Salt Effect.—Although the reproducibility of the constants listed in column 7 of Table I was fairly satisfactory, there were a few isolated cases with unexpectedly large percentage deviations, in which a high constant seemed to be correlated with high potassium iodide concentration. The data of all pairs of runs in which the iodide concentrations differed by 0.03 *M* or greater are presented in Table II. Column 2 gives the constants from col. 7, Table I, while col. 3 lists the corresponding iodide concentrations. Column 4 shows the percentage increase in the constant associated with the increase in molality of potassium iodide listed in col. 5. Column 6 gives the percentage increase in the constant per mole increase in iodide concentration for each compound, assuming a linear relation between the constant and the iodide concentration. The average increase is $57 \pm 6\%$ regardless of the compound or temperature. We have deemed it advisable to correct all of the constants of Table I to a constant iodide concentration (0.25 *M*) before calculating heats of activation (col. 8). These pairs of constants show an average average deviation of 0.55% and a maximum average deviation of 1.3%.

TABLE II
THE EFFECT OF SALT CONCENTRATION ON THE RATE CONSTANTS

Dibromide	<i>k</i> corr.	Molal concn. of KI	$\frac{100 \Delta k}{av. k}$	Δ KI	$\frac{100 \Delta k}{k \Delta KI}$
<i>cis</i> -2-Pentene	0.0564	0.232	2.1	0.040	52
75°	.0576	.272			
<i>cis</i> -2-Pentene	.01016	.257	4.0	.080	50
60°	.00976	.177			
<i>trans</i> -Crotonic acid ^a	.495	.278	2.0	.029	70
75°	.485	.249			
<i>trans</i> -Crotonic acid ^a	.1131	.283	6.1	.105	58
60°	.1064	.178			
Fumaric acid	1.189	.256	3.2	.057	56
60°	1.152	.199			
Mean (with average deviation)					57 ± 6

^a Although the study of the *cis*- and *trans*-crotonic acid dibromides is not included in this paper, these data on the *trans* isomer are given to show the consistency of the salt effect with different types of dibromides.

Preparation of Materials

All dibromides used contained the correct percentage of bromine as shown by Carius analyses.

cis- and trans-2-Pentene Dibromides.—These compounds were kindly supplied by Professor H. J. Lucas¹⁰ of the California Institute of Technology.

cis- and trans-3-Hexene Dibromides.—These compounds were prepared by the action of hydrobromic acid on the diacetates of the *meso*- and *d,l*-diethyl glycols.¹¹ The physical properties of the *cis*-3-hexene dibromide (*d,l*) were b. p. (9 mm.) 80.4–80.6°, d_{25}^{25} 1.5896, n_{25}^{25D} 1.5031, and those of the *trans*-3-hexene dibromide (*meso*) were, b. p. (9 mm.) 79.0–79.2°, d_{25}^{25} 1.5940, n_{25}^{25D} 1.5048.

cis- and trans-4-Octene Dibromides.—The dibromide of *cis*-4-octene was synthesized by Mr. Zene Jasaitis by the action of hydrobromic acid on *meso*-dipropylglycol diacetate¹²: b. p. (4 mm.) 84.0–84.5°, n_{20}^{20D} 1.4981, d_{20}^{20} 1.4569.

trans-4-Octene dibromide was obtained from a mixture of 4,4-dibromooctane and *meso*-3,4-dibromooctane which had been prepared by Mr. Leo Levanas from the racemic dipropylglycol and hydrogen bromide in the presence of zinc bromide.¹² The dibromide mixture was converted into a mixture of octane and *trans*-4-octene by reduction with zinc in alcohol. The hydrocarbon mixture, freed from alcohol, came over through a 30-cm. column of glass helices, at 119–120.3°. This distillate was treated dropwise with bromine at 0°, and the product washed with sodium bisulfite solution and with sodium bicarbonate solution and dried with calcium chloride. Fractionation through a Weston column yielded *n*-octane and a constant-boiling *trans*-4-octene dibromide, b. p. (8 mm.) 103°, n_{25}^{25D} 1.4965.

cis- and trans-Stilbene Dibromides.—A mixture of the *cis*- and *trans*-stilbene dibromides was prepared by the action of bromine on freshly distilled stilbene in carbon disulfide in the dark at 0°. The *trans*-stilbene dibromide which separated out was recrystallized twice from benzene, and dried over paraffin in a vacuum. The crystals melted with decomposition at 230–237° (reported m. p. 237°). The *cis*-stilbene dibromide was obtained from the carbon disulfide mother liquor by evaporating the solvent. The residual solid was twice recrystallized from ethanol, yielding a product melting at 109.5–111° (reported m. p. 110°).

Fumaric and Maleic Acid Dibromides.—Fumaric acid was brominated in the presence of water at 100° and the product¹⁴ melted at 270–273° after two recrystallizations from water.

Maleic anhydride and bromine were refluxed at 60–70° for two hours. The colorless reaction mixture was warmed with water, the crystals of fumaric acid dibromide were removed by filtration and the filtrate was concentrated. The first crop of crystals, m. p. 160–162°, was discarded but the second crop which formed after several weeks at room temperature (m. p. 164–167°, reported m. p. 166–167°)¹⁵ was used in this work.

Discussion of Results.—The specific reaction rate constants and the Arrhenius heats of activa-

tion for the reactions of the dibromides of several pairs of *cis-trans* isomers with potassium iodide in 99% methanol are listed in cols. 9 and 11 of Table I. In these cases in which the parent unsaturated compounds have two hydrogen atoms adjacent to the double bond and the other two groups are identical or similar the dibromide from the *trans* compound gives a greater rate constant and a smaller heat of activation than the dibromide from the *cis* isomer.¹⁶ It would appear that rate studies of this character offer a valuable method of identifying the isomers of alkene hydrocarbons which cannot be identified readily by the usual methods applied when carboxyl, amino, hydroxyl, etc., groups are present in the molecule. Until data to the contrary are obtained, therefore, it will be assumed that rate constants alone are sufficient for identifying the dibromides from *cis-trans* isomers of the type herein reported. Work on other types of stereoisomeric dibromides now in process should make it possible to establish generalizations regarding the effect of radicals on the rate constants and heats of activation.

The authors are indebted to Professor H. J. Lucas for his generosity in furnishing the *cis*- and *trans*-2-pentenenes.

Summary

The reaction of potassium iodide with several pairs of stereoisomeric alkene dibromides in 99% methanol has been investigated at 75 and 60°. A qualitative comparison of *trans*- and *cis*-stilbene dibromides in acetone indicated that the *trans* derivative reacted over a hundred times as rapidly as the *cis* derivative.

In five cases where quantitative comparisons have been made the dibromide from the *trans* parent compound of the type RHC=CHR' gave a larger rate constant and smaller heat of activation than the dibromide of the *cis* parent compound. The groups R and R' were identical or similar. Rate studies of this type have been suggested as a means of identifying *cis-trans* isomers.

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RECEIVED MARCH 1, 1939

(10) For description of these materials, see the article by Lucas and Prater, *THIS JOURNAL*, **59**, 1682 (1937).

(11) Young, Weiss and Pressman, unpublished work.

(12) Young, Jasaitis and Levanas, *ibid.*, **59**, 403 (1937).

(13) Wislicenus and Seeler, *Ber.*, **28**, 2693 (1895).

(14) Wislicenus, *Ann.*, **272**, 1 (1893).

(15) Michael, *J. prakt. Chem.*, **52**, 289 (1895).

(16) Although Davis and Heggie⁷ have pointed out that a reversal of the relative magnitude of rate constants might be observed when the reaction is carried out at different temperatures, it should be noted that the compounds which they cite, the dibromides of ethyl acrylate and maleic acid, do not possess a similarity in structure comparable to that of the stereoisomeric pairs reported in this paper. A study of the action coefficients for these and other reactions which is now almost complete will indicate whether such reversals are ever likely when dealing with stereoisomeric pairs.