and trifluoroiodomethane are judged to be unstable after numerous attempts at their preparation. Reactions of trifluorochloromethane with calcium iodide and with calcium bromide yielded carbon tetrafluoride, hexafluoroethane and iodine.

In an electric arc carbon tetrafluoride reacted with carbon monoxide to form fluorophosgene. Carbon tetrafluoride alone in an arc formed a mixture of fluorocarbons including octafluoropropane.

Iodine pentafluoride reacted with iodoform to yield fluoroform and difluoroiodomethane and with carbon tetraiodide to yield hexafluoroethane.

STATE COLLEGE, PENNA. RECEIVED SEPTEMBER 16, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

The Kinetics of the Thermal Isomerization of *trans*-Dichloroethylene

BY J. LESLIE JONES AND ROBERT L. TAYLOR*

There have been few studies made of the mechanism of homogeneous gaseous isomerization reactions. Of the studies, only those of Kistiakowsky and co-workers are quantitative. Kistiakowsky, *et al.*, have studied the gas phase isomerization of methyl maleate,[1a] methyl cinnamate,[1b] isostilbene[1c] and *cis*-butene-2.[1d] They found that the activation energy of the isomerization of dimethyl maleate to dimethyl fumarate was 26,500 cal. as compared to the values of 41,600 cal. and 43,000 cal. for the isomerization of *cis*-methyl cinnamate to *trans*-methyl cinnamate and isostilbene to stilbene, respectively. The research on the isomerization of *cis*-butene-2 to *trans*-butene-2 led to the conclusion that the reaction involved a chain mechanism. The widely separated values of the activation energies for the aliphatic ester and the aromatic derivatives were striking. In addition, the attempt to determine the mechanism of geometrical isomerization in the absence of groups contributing appreciably to resonance structures was unsuccessful, as the results obtained with the butene-2 indicated. In view of these facts, it was decided to investigate the gaseous isomerization of *trans*-dichloroethylene.[2]

This molecule represents the simplest example of a *cis–trans* isomer with significant differences in the physical properties of the two isomers. The contribution of resonance structures to the strength of the double bond is a minimum. Wood and Dickinson[3] recently published a study of the iodine catalyzed isomerization of the *trans* form in the liquid phase and in solution, but the research cast no light upon the simple thermal isomerization mechanism.

Experimental Section

Preparation of Dichloroethylene.—The *trans*-dichloroethylene used in this work was obtained in a fairly pure form from the Eastman Kodak Company. It was further purified by repeated fractionation in a three-foot column, packed with glass helices. Starting with 1500 cc. of material, 400 cc. was obtained with a boiling point range of 47.85 to 47.87° at 769.5 mm. pressure. The *cis* isomer was prepared by treating 300 g. of the *trans* form with 18 g. of bromine and allowing it to stand in the dark for twenty-four hours. The resulting equilibrium mixture was washed with 10% potassium hydroxide, several portions of distilled water dried over calcium chloride and fractionally distilled. About 40 cc. of *cis*-dichloroethylene was obtained which boiled at 59.9° at a pressure of 768.0 mm. (boiling range less than 0.1°). The boiling points obtained by Wood and Dickinson[3] were 59.6° for the *cis* isomer and 47.2° for the *trans* isomer at 745 mm. pressure.

Apparatus.—The apparatus used in the experimental study was the static type, employing a quartz spiral manometer as a null point indicator. A Pyrex glass hollow-barrel stopcock was employed to close the reaction vessel and was greased with a high melting lubricant. This particular stopcock together with the small amount of capillary tubing extending out of the furnace was heated with nichrome wire to prevent condensation of dichloroethylene. The reaction vessel was enclosed in an aluminum sheathing within the furnace in order to minimize temperature gradients and a thermocouple inserted into the sheathing. The alumel–chromel thermocouple was calibrated against condensing naphthalene and benzophenone. The temperature was usually constant within ±0.1°.

Because of the possible reaction between mercury vapor and dichloroethylene, particular precautions were taken to

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* A portion of this material is taken from the thesis submitted by Robert L. Taylor in partial fulfillment of the requirements for the Master of Science degree in chemistry.

(1) (a) Kistiakowsky and Nelles, *Z. physik. Chem.*, *Bodenstein Festband*, **152**, 369 (1931); Kistiakowsky and Nelles, THIS JOURNAL, **54**, 2208 (1932); (b) Kistiakowsky and Smith, *ibid.*, **57**, 269 (1935); (c) Kistiakowsky and Smith, *ibid.*, **56**, 638 (1934); (d) Kistiakowsky and Smith, *ibid.*, **58**, 766 (1936).

(2) Ebert and Bull, *Z. physik. Chem.*, **A152**, 451 (1931), announced that they intended to study the kinetics of the gaseous isomerization, but no results have been published to date.

(3) Wood and Dickinson, THIS JOURNAL, **61**, 3259 (1939).

prevent the mercury vapor from entering that section of the system where the dichloroethylene was stored or the reaction vessel. Thus any side reaction due to mercury may be excluded.

A 500-cc. Pyrex spherical flask packed with short lengths of Pyrex glass tubing was used to determine the homogeneity of the reaction. The unpacked 500-cc. flask was used in all experiments and had a surface–volume ratio of 0.55 cm.$^{-1}$ and the packed flask a ratio of 7.3 cm.$^{-1}$

Analysis of the Reaction Products.—The rate of the reaction was followed by allowing the *trans* material to react for definite time intervals, removing the product, and analyzing the resulting material for the per cent. of each isomer. The best available method of analysis was by means of a Pulfrich refractometer, using sodium D light. The value of n^{25}_D for the pure *trans* isomer was 1.43969 and that of the *cis* isomer 1.44284—a difference of 0.00315. The accuracy of reading was ±0.00001, which gave an accuracy of analysis of almost 0.5%. As little as 0.15 cc. of material could be analyzed. A calibration curve was prepared by using known mixtures of the two isomers and plotting the refractive index against the per cent. of the *cis* isomer, at constant temperature. This curve is shown in Fig. 1. The greatest difficulty in the analysis was found to be due to variations of the room temperature. This difficulty was minimized by running water from a thermostat, regulated to 25 ± 0.05°, through the instrument, and by correcting each reading by the amount of variation of the pure *trans* reading. This latter correction was made by making a reading on pure *trans*-dichloroethylene after each analysis and using the difference between this reading and that of pure *trans* on the calibration curve as a correction.

Experimental Results

There is no doubt that the reaction involved in this study is the isomerization of *trans*-dichloroethylene to the *cis* form. Ebert and Bull reported preliminary results on a study of the thermal equilibrium involved, giving a value of 63% *cis* form for the equilibrium mixture at 300°. They gave no evidence indicating decomposition. Olson and Maroney[4] carried out extensive studies on the photochemical and thermal equilibria. Greater reliability can be placed upon their data, which gave the thermal equilibria concentration of *cis* form as 60.8% at 300° and 59.4% at 350°. The data were used in this study to provide a simple logarithmic curve for the variation of the equilibrium constant with the temperature.

Dichloroethylene proved to be very stable with respect to decomposition. In some of the experiments at higher temperatures, with an untreated flask or packing, there was a slight increase in pressure. This only occurred on initial overnight experiments. In experiments in which the time ranged from a few minutes to several hours the pressure increase was always less than 1 mm. Hydrogen chloride was shown to have formed in the longer runs but this did not affect the analysis. A sample of pure *trans* dichloroethylene was saturated with hydrogen chloride gas and the refractive index changed by an amount corresponding to a 2% change in composition. It is logical to assume that the small amount of hydrogen chloride formed in any experiment would not affect the analysis. The refractive indices of products of overnight experiments corresponded to 85–97% *cis*. This was assumed to be due to the formation of a volatile product of the side reaction, which condensed with the dichloroethylene and registered in the analysis as the *cis* isomer.

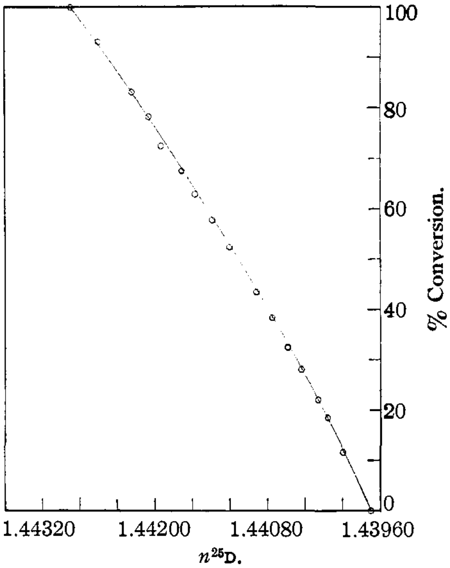

Fig. 1.

It was necessary to treat the reaction flask from one to three days, after exposing the surface to air, in order to obtain reproducible results. After the treatment of the flask, a dark deposit of carbon or polymerized compound coated the surface and decreased the reaction rate to a constant value. The reacting substances were then no longer in contact with a glass surface, but a surface of the polymer. When a packed flask was substituted, this treatment had to be extended to almost a week. The reaction vessel was exposed to an atmosphere of pure oxygen overnight and the experiments immediately following gave very high rate constants, indicating that oxygen markedly affected the nature of the surface coating. Similar increases in the rate constants were noticed whenever air leaked into the system.

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[4] Olson and Maroney, THIS JOURNAL, 56, 1320 (1934).

The rate constants for the isomerization were calculated by the unimolecular equation

$$k = \frac{1}{(t + 1/K)} \ln \left[\frac{100}{100 - (1 + 1/K)x}\right]$$

where x was the % of *trans* in the condensate removed from the system after time t. K was equal to the equilibrium ratio (*cis*)/(*trans*). This equation assumed that both the forward and reverse reactions were unimolecular. The temperature range found most suitable for the kinetic study was from 560 to 608°K. The pressure range was from 200 mm. to one atmosphere. At pressures much below 200 mm. the amount of product condensed was not sufficient for analysis, while pressures above one atmosphere could not be read on the mercury manometer.

In Table I are given typical values of k at the various experimental temperatures. The total number of experiments was 184. The results of some runs were excluded because of error due to surface effects from exposure of the flask to air or mishaps in removal of the material for analysis. The runs in the packed flask numbered 11. Lack of space precludes tabulation of all pertinent experimental results.

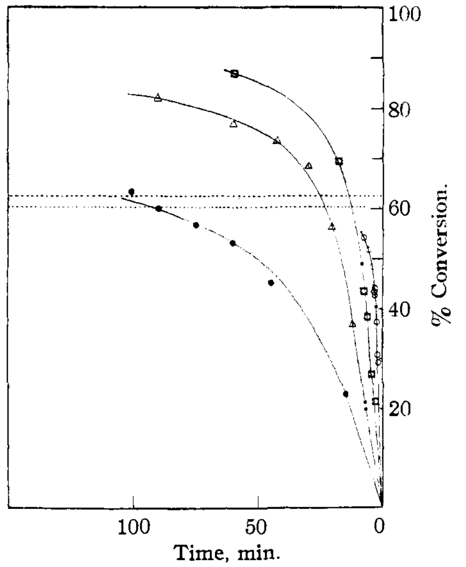

Fig. 2.—●, unpacked flask at 562.5°K.; △, packed flask at 560.0°K.; □, packed flask at 578.0°K.; ○, unpacked flask at 608.0°K.

Some sets of experiments indicated a falling off of the rate constant with the decreasing pressure, while others were contradictory in this respect. Experiments at 606.5°K. and 566.0°K. showed a slight decrease in rate with falling pressure; runs at 591°K. showed a tendency for the same but were inconsistent; and those at 562.5°K. were altogether out of accord. Results indicate that the runs of shorter time varied with pressure and agreed more closely among themselves. They were probably the more accurate. For this reason it is very probable that there was a slight decrease in the rate constant with the decreasing pressure in this pressure range.

Table I

No.	Temp., °K.	Pressure, mm.	Time, sec.	$k \times 10^4$ (sec.$^{-1}$)
127	607.5	280	300	39.5
128	607.5	310	350	41.5
129	607.5	366	180	41.9
106	591.5	255	480	14.7
107	591.5	249	480	15.3
108	591.5	245	480	14.7
92	585.5	261	600	9.19
93	585.5	227	840	8.01
94	585.5	642	841	9.01
44	562.5	420	3600	2.60
45	562.5	217	3600	2.31
46	562.5	759	3600	3.24

The surface volume ratio was 13.2 times as great in the packed flask as in the unpacked flask. In Fig. 2 the per cent. conversion into the *cis* isomer is plotted against time for corresponding temperatures, for the packed and unpacked flasks. The composition at equilibrium is enclosed in the horizontal dotted lines. The curve representing the packed flask does not appreciably decrease in slope near the true equilibrium, but continues far past this equilibrium position. Since it is impossible for the per cent. of *cis* isomer formed in any reaction to be greater than that represented by the equilibrium composition, the rapid rise of the curve must be largely due to the presence of the product of the side reaction, which registers in the analysis as *cis*-dichloroethylene. This means that the side reaction of decomposition was increased to a greater extent by packing than the reaction of isomerization. The curves for the unpacked flask, even at higher temperatures, show a much greater change in slope in the region of equilibrium than the curves for the packed flask, even at lower temperatures. This indicates that the isomerization process is probably heterogeneous to some extent but small in comparison to that of the side reaction. The accuracy of the experiments of shorter time can be understood in view of the slowness of the side reaction in the unpacked flask.

The data used in calculating the activation energy E and the temperature independent factor A in the Arrhenius equation are shown in Table II. The average values of k (neglecting the pressure effect on k) for the various temperatures investigated, are tabulated, together with the average deviation, and the number of experiments averaged given in column 3. The values of k in experiments up to 37 were not included due to the omission of a correction for the temperature variation in the analysis. Experiments 61 through 69 were excluded, for in these runs the product was evacuated after freezing. Differential evaporation probably took place in these cases, giving high values for k. Runs 69 to 72 were made after exposing the flask to pure oxygen overnight, and were therefore omitted. The values given in Table II were plotted in Fig. 3. The activation energy, obtained from the slope of the straight line drawn through most points, was 41,900 cal. The maximum error in this value was calculated to be ±4.5 kcal. Using this value of E, the temperature independent factor is given by 4.9×10^{12}, and the results of the investigation can be represented by the equation

$$k = 4.9 \times 10^{12} e^{-41,900/RT} \text{ sec.}^{-1}$$

It should be mentioned that the senior author studied the gaseous isomerization of the reverse reactions, *i. e.*, conversion of *cis*-dichloroethylene to the *trans* form. The apparatus and technique were very similar to those previously described, but the results were not consistent with those reported here. There was no visible indication of deposition of a carbonaceous layer on the surface of the reaction vessel. The values of the rate constants varied with the time of treatment of the flask with dichloroethylene. The activation energy could not be calculated accurately and was estimated as 27,000 to 37,000 calories. The difference in the behavior of the two isomers was probably directly related to the formation of a heavy carbonaceous layer on the reaction vessel in the case of the *trans* form thus effectively changing the nature of the reaction vessel surface. It seemed reasonable to consider the above reaction as heterogeneous.

TABLE II

UNPACKED FLASK

Temp., °K.	Average value of k, sec.$^{-1}$	No. of runs
562.5	2.55 ± 0.51	15
565.5	4.85 ± 0.50	2
566.0	5.56 ± 0.47	3
575.0	6.65 ± 0.37	4
580.5	8.83 ± 1.12	3
585.5	8.76 ± 1.11	12
586.0	12.8 ± 0.2	5
588.0	15.1 ± 0.4	6
591.0	11.4 ± 0.5	6
591.5	14.9 ± 0.3	3
600.0	26.2 ± 0.5	3
603.0	31.1 ± 0.4	4
606.5	37.9 ± 0.8	3
607.5	40.9 ± 1.0	3
608.0	42.8 ± 0.7	4
	Packed Flask	
560.0	6.84 ± 0.72	7
578.0	15.4 ± 0.5	4

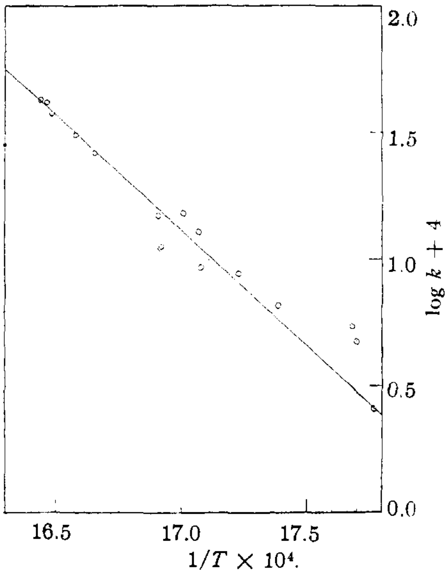

Fig. 3.

Discussion

It seems useless to apply the theory of Rice–Ramsperger–Kassel to the falling off of the rate constant with pressure, due to insufficient data. Since the maximum number of internal degrees of freedom possible in the molecule is 12, the large value of the temperature independent factor probably indicates a high degree of participation by these degrees of freedom in the reaction. As to be expected, the number of internal degrees of freedom participating in the reaction is the same order of magnitude as for stilbene (12) and methyl cinnamate (6).

The activation energy calculated for the isomerization of *trans*-dichloroethylene is the same as that determined for the methyl cinnamate and stilbene isomerization (*i. e.*, *ca.* 42,000 cal.). This value is significantly different from the value of 26,500 cal. obtained for the isomerization of methyl maleate. The contribution of resonance structures to the strength of the double bond in dichloroethylene is appreciable,[5] but certainly not an important factor in determining the strength of the double bond. The similar values of the activation energy for molecules so dissimilar with respect to stabilization of bonds by resonance, leads one to the conclusion that resonance plays little if any part in the isomerization mechanism.[1b] The same evidence is indicative of the minor role that mechanical rotation probably plays in the isomerization of dimethyl maleate.[1b] The reaction mechanism responsible for the isomerization of dimethyl maleate is essentially different from that of the other geometrical isomers. As proposed by Conant,[1a] the ester exists in tautomeric states and the enolic state is capable of yielding either the fumarate or maleate esters. The rate of tautomerization is thus the slow rate-determining step and would be expected to have a much lower activation energy than the other postulated mechanisms. Such a mechanism is usually associated with a heterogeneous reaction or a reaction occurring in a polar solvent, but no evidence conclusively bars it from present consideration in the case of compounds capable of undergoing enolization. The study of a simple aliphatic ketone which can exist as a geometrical isomer obviously suggests itself as a possible means of testing this conclusion.

Olson[6] has advanced the theory which accounts for the similar activation energies of the cinnamate, stilbene and dichloroethylene molecules. The activation energy accumulates in the necessary degrees of freedom, resulting in a loosening of the carbon–carbon double bond in one linkage, the two tetrahedra remaining joined together by a single bond. Rotation about this bond is followed by an inversion of one of the free valence bonds of one of the carbon atoms. The reformation of a double bond and subsequent loss of the excess energy by collision completes the reaction. On this basis the energy required for activation is localized in the internal degrees of freedom of the double bond and the amount of energy is independent, to a large extent, of the nature of the attached atoms. It would obviously be desirable to test this mechanism by a direct method such as the Paneth lead mirror technique. However, the known reactivity of alkyl halides with metals makes any such experiment meaningless.

Statistical calculations based upon Eyring's theory of unimolecular reactions[7] substantiate the above hypothesis. The so-called "frequency factor" is calculated from the equation

$$k = c^* \frac{\sigma}{\sigma^*} \left(\frac{A^*B^*C^*}{ABC}\right)^{1/2} \prod_{i=1}^{3n-7} (1 - e^{-h\nu^*/kT})^{-1} \times \prod_{i=1}^{3n-6} (1 - e^{-h\nu/kT}) \frac{kT}{h} e^{-E_0/kT} \quad (2)$$

where the symbols have their usual significance. Since the chemical evidence supports the conclusion that essentially the carbon–carbon double bond is the only bond involved in the isomerization, the calculation of the "frequency factor" is simplified. In effect, the double bond becomes a single bond in the activated complex and free rotation is assumed to occur. The bond distances and frequencies of the other linkages remain unchanged in the activation process.

For the normal *trans*-dichloroethylene molecules the following constants are employed[8]: C=C distance, 1.38 Å.; C–Cl distance, 1.69 Å.; C–H distance, 1.12 Å.; C–C–Cl angle, 122.5°, C–C–H angle, 109.5°. Four vibrational degrees of freedom are attributed to the carbon–carbon double bond, one stretching, one torsional and two bending vibrations with frequencies of 1575, 752 and 350 cm.^{-1}, respectively.[9] A symmetry number of two is assumed.

In the activated complex the carbon–carbon distance is assumed to be that of a single bond, 1.54 Å. The other distances and angles are considered unchanged. In any event, reasonable differences will not change the frequency factor by more than twofold. A symmetry number of two is assumed for the activated complex. One carbon–carbon stretching vibrational frequency of 1000. cm.^{-1} and two bending frequencies of 950 cm.^{-1} are attributed to the activated complex single bond.

Using the given molecular constants, the three moments of inertia for the normal molecule are calculated as 16.0, 320 and 563 $\times 10^{-40}$, while they are 16.0, 357 and 599 $\times 10^{-40}$ for the activated complex. Substitution in equation (2) yields a value of 4.85 $\times 10^{12}$ for the frequency

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[5] *Cf.* Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 200.

[6] Olson, *J. Chem. Phys.*, **1**, 418 (1933); THIS JOURNAL, **56**, 1320 (1934).

[7] Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

[8] Pauling, Beach and Brockway, THIS JOURNAL, **57**, 2693 (1935).

[9] Hibben, *Chem. Rev.*, **18**, 32 (1936).

factor as compared with the experimental value of 4.9×10^{12}. Such close agreement is regarded as fortuitous, but substantially supports the theory proposed to account for the isomerization. The introduction of hindered rotation in the activated complex to the extent of about 3000 calories would result in an increase in the frequency factor by about 1.2 fold. In addition, the activated complex possesses two unshared electrons capable of forming singlet and triplet states. This probably leads to an electronic multiplicity factor of four for the activated complex, which of course increases the frequency factor fourfold. In any event the frequency factor has been calculated within a factor of fivefold and thus justifies serious consideration of the Olson theory as an explanation for all geometrical isomerization reactions incapable of proceeding by tautomerization.

An obvious corollary of this theory is the proposition that 43,000 calories represents the energy required to open the carbon–carbon double bond in a molecule. The values obtained for structurally different molecules support this figure.

Summary

The thermal isomerization of gaseous *trans*-dichloroethylene into the *cis* form was found to be approximately homogeneous and of first order in the temperature range of 566 and 608°K. A pressure range of 700 to 200 mm. was investigated. The rate of the reaction was expressed by the equation

$$k = 4.9 \times 10^{12} e^{-41,900/RT} \text{sec.}^{-1}$$

The activation energy compared favorably with those found by Kistiakowsky for the isostilbene and methyl cinnamate isomerizations.

A mechanism is proposed to account for the isomerization of geometrical isomers. The isomerization is a consequence of the activation of the carbon–carbon double bond to form a single bond with two free valences. Free rotation of the H–C–Cl groups takes place and a double bond is reformed in the *cis* molecule by an inversion of a free carbon valence.

WASHINGTON, D. C. RECEIVED AUGUST 26, 1940

[CONTRIBUTION FROM THE LABORATORY OF BIOLOGICAL CHEMISTRY, SCHOOL OF MEDICINE, UNIVERSITY OF BUFFALO]

The Rates of Reaction of the Stereoisomeric Oximes of Cholestenone and of Benzal-*p*-bromoacetophenone with Iodine Monobromide

BY J. O. RALLS

Introduction

Among the many manifestations of steric hindrance, we are concerned only with steric hindrance effects in the reactions of certain types of stereoisomers. Some interesting observations have been made upon the rates of esterification and of hydrolysis of *cis* and *trans* isomers of cyclopentanols[1] and cyclohexanols[2,3] and the influence of steric hindrance in those cases. In general, the *trans* form esterified and hydrolyzed the more rapidly. Steric hindrance seemed to modify, also, the rates of hydrolysis of[4] esters of *cis* and *trans* cinnamic acid and[5] of certain stereoisomeric hydrazones and oximes. The *anti* oximes hydrolyzed considerably more rapidly than did the *syn* oximes. More pertinent, however, are the observations of Merz[6] on the rates of hydrogenation of the oximes of isovanillalacetone (α,β unsaturated ketone). He observed that the *syn* form was, whereas the *anti* form was not, readily hydrogenated. Since the relation between oxime configuration and the Beckmann rearrangement was not fully clarified until a year later,[7,8] it is probable that his *syn* and *anti* designations were in error.

In a previous paper,[9] the author suggested that the failure of cholestenoneoxime to halogenate in glacial acetic acid and its easy halogenation in carbon tetrachloride could be due to the existence of one form (*syn*) in one solvent and of another form (*anti*) in the other solvent. This was contrary to the belief of K. v. Auwers[10] that the addition of halogen to α,β unsaturated ketoximes

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[1] Vavon and Flurer, *Bull. soc. chim.*, **45**, 754–762 (1929).

[2] Vavon and Mitchovitch, *ibid.*, **45**, 961–972 (1929).

[3] Vavon and Guedon, *ibid.*, **47**, 901 (1930).

[4] Manta, *ibid.*, **53**, 1277–1286 (1933).

[5] Johnson and Stieglitz, THIS JOURNAL, **56**, 1904 (1934).

[6] Merz, *Ber.*, **63B**, 2951–2953 (1930).

[7] Blatt, THIS JOURNAL, **53**, 1133 (1931).

[8] Blatt and Stone, *ibid.*, **53**, 4134 (1931).

[9] Ralls, *ibid.*, **60**, 1748 (1938).

[10] K. v. Auwers and Muller, *J. prakt. Chem.*, **137**, 65–66 (1933).