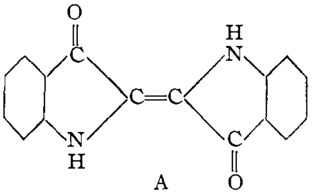
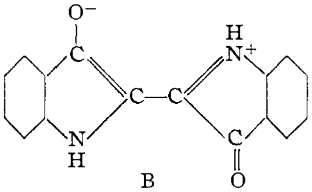
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Freedom of Rotation about the Carbon–Carbon Double Bond. Certain Substituted Stilbenes

BY MELVIN CALVIN AND ROBERT E. BUCKLES

It has long been known that the difficulty of the thermal *cis–trans* isomerization about the carbon–carbon double bond may vary greatly depending on the groups attached to the ethylenic center. This has been demonstrated in a quantitative way in a number of isolated cases in which the activation energy for the thermal *cis–trans* isomerization has been found to vary from 46 kcal.[1] down as low as approximately 30 kcal.[2] There is no reason to expect that this value may not be lowered still more by proper substitution until the point is reached at which the resistance to rotation about the double bond is so low that isomerization would take place readily at room temperature and the isolation of a pair of isomers would become impossible. This seems to be the case in the well-known problem of the structure of indigo, which is normally written as containing a double bond formally capable of exhibiting *cis–trans* isomerism but for which until recently only one substance could be prepared. The new isomer of indigo is, however, very unstable and reverts to the normal form in a few hours even in the solid state.[3] This lack of stable isomerism in indigo and the ability of indigo to undergo reactions which would normally be attributed to both *cis* and *trans* forms has led to the suggestion by van Alphen[4] that the actual ground state of the indigo molecule is a resonance hybrid involving the forms A, B, and C.


A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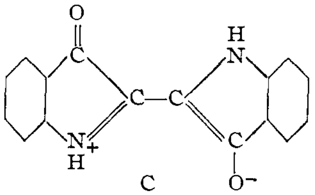
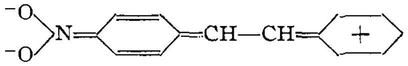

C

Since the forms B and C have a single bond in place of the double bond about which the isomerism is to take place, the resistance to rotation about this bond will be diminished with increase in the magnitude of the contribution of the forms B and C to the ground state of the molecule. A similar suggestion has been offered by E. Bergmann[5] to account for the apparent impossibility of preparing two isomers of 2,2′-difluorodibiphenyleneethylene and its dipole moment[6] of 2.5 *D* which lies between the expected values of 0 and 2.90 for the *trans* and *cis* compounds, respectively.

In order to gain some insight into the mechanism of the influence of those structural factors of the molecule surrounding the double bond, on the ease or difficulty of rotation about its axis, it was decided to investigate the series of substituted stilbenes starting with the para, mono and disubstituted compounds. From many other sources[7] we have reason to know that the ground states of the molecules *p*-nitrostilbene (I) and *p*-aminostilbene (II) must have considerable contribution from the resonance states D and E, respectively,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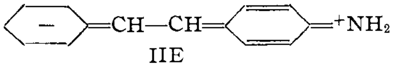
IIE

and, furthermore, in 4,4′-aminonitrostilbene (III) the contribution of the resonance form F is greater than would be expected on the basis of simple addition of the mononitro and monoamino compounds.

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[1] G. B. Kistiakowsky and W. R. Smith, THIS JOURNAL, **58**, 2428 (1936).

[2] M. Calvin and R. E. Buckles, unpublished estimate from observation on 4,4′-dinitrostilbene in the pure liquid phase.

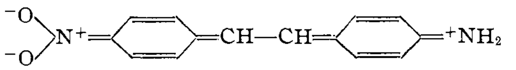
[3] G. Heller, *Ber.*, **72**, 1858 (1939).

[4] J. van Alphen, *ibid.*, **72**, 525 (1939).

[5] E. Bergmann, private communication.

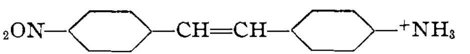
[6] E. Bergmann, *J. Chem. Soc.*, 987 (1935).

[7] For a detailed discussion of these sources and their interpretation see "The Theory of Organic Chemistry," G. E. K. Branch and M. Calvin, published by Prentice-Hall, Inc., New York (autumn-winter, 1940).



IIIF

If, however, a proton is added to the base, III, to form the ammonium ion IV



IV

the resonance F is completely blocked and the residual contributions of the type of D to the salt ion IV are reduced below what they would be in the nitro compound I by the presence of the positive charge on the right-hand ring of IV. Thus, 4,4′-aminonitrostilbene represents an extreme case in which the substituents might so greatly reduce the barrier to the rotation about the double bond as to make the isolation of the two geometric isomers very difficult or impossible under normal conditions. It is to be expected, however, that the isomeric salts will be very much more stable, having a stability comparable with that of the *p*-nitrostilbene. These expectations have been entirely fulfilled by the following experiments.

An attempt was made to prepare the isomeric *p*-aminonitrostilbenes by careful partial reduction of the *cis*- and the *trans*-4,4′-dinitrostilbene with sodium sulfide, hydrogen sulfide in alcoholic solution. The identical aminonitro compound was obtained from both reductions. Its melting point is 245°. In addition to the aminonitro compound a small amount of 4-ethylamino-4′-nitrostilbene was also formed in both reductions. Complete reduction of both *cis* and *trans* forms of the dinitro compound by either sodium sulfide, hydrogen sulfide, or by tin and hydrochloric acid yielded only the *trans*-*p*,*p*′-diaminostilbene.

When the base, III, is dissolved in hot aqueous hydrochloric acid and permitted to recrystallize on cooling two apparently isomeric salts are obtained depending on the acidity (or ionic strength) of the solution. From acid solutions between 0.25 *N* and 0.6 *N* a red salt is crystallized, while from solutions 1 *N* and 2 *N* in hydrochloric acid a yellow salt is obtained. Furthermore, this seems to be an ionic strength effect since crystallization from a solution 0.25 *N* in hydrochloric acid and 3.5 *N* in sodium chloride produces the yellow salt. It is not an effect of the activity (thermodynamic) of the acid since the activity of the hydrochloric acid in 0.6 *N* acid is somewhat greater than it is in the 0.25 *N* acid containing 3.5 *N* sodium chloride.

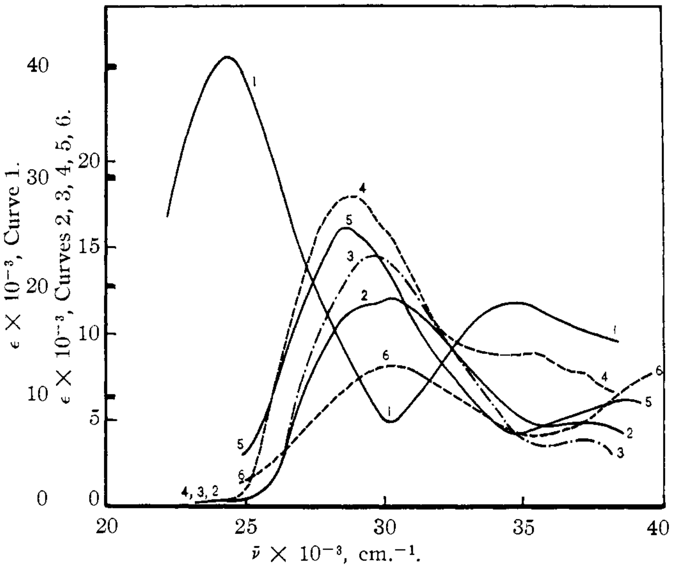


Fig. 1.—Absorption spectra of *p*,*p*′-aminonitrostilbene and *p*-nitrostilbenes in absolute alcohol: (1) *p*,*p*′-aminonitrostilbene; (2) with 4.8×10^{-4} *N* HCl; (3) with 4.8×10^{-3} *N* HCl; (4) with 3.0 *N* HCl; (5) *trans*-*p*-nitrostilbene; (6) *cis*-*p*-nitrostilbene.

These facts lead to the question of whether there is any difference in the molecular species in solution at the various acidities and, if so, what this difference is. This was investigated by obtaining the absorption spectra of the base, III, in solutions of varying acidity and comparing these with the absorption spectra of the *cis* and *trans* *p*-nitrostilbene which would be expected to be very similar to those of the salts.[8] The spectra were made on alcoholic solutions since the solubilities of both the salts and the *p*-nitro compounds in dilute acid or water was too small. A solution of the free base in absolute alcohol shows two bands, shown in Fig. 1, one of high intensity at 4095 Å. and one of much lower intensity at 2890 Å. In a solution in absolute alcohol which is 4.8×10^{-4} *N* in hydrochloric acid the absorption of the free base (bands at 4095 and 2890 Å.) are completely lacking and a new band has appeared at 3310 Å. If the acid concentration is raised to 3 *N* the new band (due to the salt ion) moves to 3470 Å. and is somewhat increased in intensity. An intermediate acid concentration shows a band of intermediate wave length and intensity. A comparison of these absorption spectra with those

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[8] G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 309 (1939).

of *cis* and *trans* *p*-nitrostilbene, shown in Fig. 1, shows a very striking correspondence between the absorption in low acid concentration (10^{-4} *N*) with that of *cis*-*p*-nitrostilbene whose band is at 3290 Å., and the absorption in high acid concentration (3 *N*) with that of *trans*-*p*-nitrostilbene.[9]

Experimental Part

Preparation of *trans*-4,4′-Dinitrostilbene.—This preparation was carried out according to the method of Walden and Kernbaum[10] from *p*-nitrobenzyl chloride in alcoholic potassium hydroxide. The crystals were yellow needles which melted at 296–305°.

Preparation of *cis*-4,4′-Dinitrostilbene.—By condensation: *p*-nitrobenzaldehyde according to Ruggli and Lang.[11] A very poor yield of light yellow plates was obtained, m. p. 184.5–187.5°. By illumination: 13.5 g. of the *trans*-4,4′-dinitrostilbene was dissolved in 450 cc. of hot nitrobenzene. The solution was illuminated for fifty hours by two quartz mercury arcs, each drawing 3.5 amp. at 220 volts. The illumination was carried out at 80–90° in a Pyrex flask with a capillary to prevent vapor diffusion. At 90° all the *trans* form is not in solution, but at the end of the radiation it had dissolved. Some decomposition was indicated by a darkening of the solution. Cooling the solution crystallized out the *trans* form. Subsequent crystallizations followed the concentration of the solution by means of steam distillation. This avoided the possibility of isomerization at high temperatures. When the volume reached about 5 cc. the *cis* form precipitated. The yields were 8.4 g. *trans* and 3.5 g. *cis*. This is 29% *cis* of the recovered product or 26% of the starting material. Further purification was accomplished by recrystallization first from nitrobenzene and then from acetone. The very light yellow plates melted at 183–185°. A mixed melting point with the product by condensation gave no lowering. It should be noted in giving these melting points that due to isomerization the melting point decreases and then rises again as the bath is held at temperatures around 200°. The *cis* form was converted to the *trans* by boiling in acetone with a trace of iodine.[11]

Preparation of 4-Amino-4′-nitrostilbene.—The preparation of this compound using ammonium sulfide to reduce 4,4′-dinitrostilbene[12] did not work satisfactorily. Instead sodium sulfide solution saturated with hydrogen sulfide was used.[13] Ten grams of *trans*-4,4′-dinitrostilbene (0.037 mole) was suspended in 400 cc. of 95% alcohol and heated to boiling on a steam-bath. Then 26 cc. of a 1.25 *M* solution of sodium sulfide saturated with hydrogen sulfide was added a little at a time. The solution turned dark red. It was allowed to evaporate to dryness. The residue was extracted with acetone and the extract evaporated to dryness. The residue was then recrystallized from nitrobenzene in the same manner as was the *cis*-4,4′-dinitrostilbene. Two compounds appeared: one, dull red, melted at 245–245.5°; the other, glistening red plates, melted at 222–223°. The former was predominant, being about 60% of the theoretical yield. It is the 4-amino-4′-nitrostilbene. The other is believed to be 4-ethylamino-4′-nitrostilbene.

Anal. Low melting: calcd. for $C_{16}H_{16}N_2O_2$: N, 10.45. Found: N, 10.03. High melting: calcd. for $C_{14}H_{12}N_2O_2$: N, 11.67. Found: N, 11.26.

If twice the amount of reducing solution is used the *trans*-4,4′-diaminostilbene is formed, m. p. 228–229.5°. This is also the case if excess sodium sulfide solution is used.

The partial reduction as described above was carried out on the *cis*-4,4′-dinitrostilbene. The 4-amino-4′-nitrostilbene obtained melted at 244–244.5° and the ethylamino compound melted at 222.5–223°. The reaction was faster on the *cis* compound.

The Salts of 4-Amino-4′-nitrostilbene.—Strakosch[12] describes the crystallization of the salt from alcoholic hydrochloric acid. He describes only one, however. If the nitroamino free base is dissolved in hot 0.5 *N* hydrochloric acid reddish-gold plates precipitate on cooling and after standing a small amount of another substance, yellow needles, comes down. If the base is recrystallized from 0.25–0.5 *N* hydrochloric acid the product is almost exclusively the red salt. From 1.0–2.0 *N* the yellow salt is the product. Starting with either salt, it can be converted to the other by recrystallizing from the correct acid solution. Either salt is converted to the same free base (m. p. 245–246°) by water, alkali, or even 0.1 *N* hydrochloric acid. Both salts decompose starting at about 230° and melt completely at 245°. *Anal.* Red salt, calcd. for $C_{14}H_{13}N_2O_2Cl$: N, 10.15; Cl, 12.87. Found: N, 10.31; Cl, 11.28. Equiv. wt. as an acid, calcd. for $C_{14}H_{13}N_2O_2Cl$: 276. Found: 300. Yellow salt, found: N, 10.08; Cl, 14.24; equiv. wt., 260.

The red salt was prepared in relatively large quantities starting from the free base in acetone solution.

Effect of Sodium Chloride on the Crystallization of Hydrochloride Salts of 4-Amino-4′-nitrostilbene.—A solution 0.25 *N* in hydrochloric acid, 0.002 *N* in the stilbene hydrochloride and 3.5 *N* in sodium chloride, gave crystals of the yellow salt. Some were even precipitated by a salting out action during the boiling after the sodium chloride solution had been added.

A solution 0.6 *N* in hydrochloric acid and about 0.002 *N* in the stilbene salt precipitated the red salt on cooling.

Reduction of Both Nitro Groups of *cis* and *trans* 4,4′-Dinitrostilbene.—Complete reduction of the 4,4′-dinitro- to the 4,4′-diaminostilbene is best carried out with tin and hydrochloric acid.[14] 0.3 g. (0.0011 mole) of each of the *cis* and *trans* 4,4′-dinitrostilbene was suspended in 20 cc. of 95% alcohol and heated on a steam-bath. When boiling started, 1 g. of tin metal and 4 cc. of concentrated hydrochloric acid, making it 2 *N*, were added to the solution. It was two hours before the suspended matter dissolved, indicating the reaction was completed. The solutions were treated with aqueous sodium hydroxide and boiled in order to dissolve the tin hydroxides. The crude bases thus formed were, for the *cis*, 0.19 g., melting at

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(9) This band corresponds very well with that reported by E. Hertel and H. Lührmann, *Z. physik. Chem.*, **B44**, 261 (1939), in which the absorption spectra of a number of stilbenes is reported without any indication of which isomer was used.

(10) P. Walden and A. Kernbaum, *Ber.*, **23**, 1959 (1890).

(11) P. Ruggli and F. Lang, *Helv. Chim. Acta*, **21**, 38–50 (1938).

(12) J. Strakosch, *Ber.*, **6**, 328 (1873).

(13) Stoermer, "Die Methoden der organischen Chemie," Houben–Weyl, Vol. 11, pp. 378–381, Verlag Georg Thieme, Leipzig, 1930.

(14) Elbs and Hoermann, *J. prakt. Chem.*, [2] **39**, 502 (1889).

182–184° (or purifying through the salt it melted at 224–227°), and for the *trans*, 0.19 g., melting at 222–224°. If the reaction is run with the *trans* compound, using 23 cc. of alcohol and 1 cc. of the hydrochloric acid, making it 0.5 *N*, the reaction is faster (one and one-half hours) and the product is purer, 0.21 g.; m. p. 227–228°. The melting point of the *trans* 4,4′-diaminostilbene is 227–228°[14] and that of the *cis* form is 121°.[11]

Reduction of the 4-Amino-4′-nitrostilbene.—0.3-g. (0.001 mole) samples of one or the other of the salts of 4-amino-4′-nitrostilbene were dissolved in 250 cc. each of 0.5 *N* and 1.0 *N* hydrochloric acid. When they started boiling 0.5 g. of tin metal was added and the boiling continued for one and one-half hours; m. p. of the crude bases obtained from 0.5 *N* hydrochloric acid, 200–204°, and from 1.0 *N* hydrochloric acid, 210–220°.

Preparation of *trans*-4-Nitrostilbene.—The method of preparation is that of Pfeiffer and Sergiewskaja.[15] Sixteen grams of *p*-nitrophenylacetic acid, 9.20 g. of benzaldehyde and 4 cc. of piperidine were permitted to react for four hours at 150–160°. The residue was extracted with toluene and given six treatments with charcoal. The resulting solution was still dark, but concentrating and cooling it brought down yellow crystals which were recrystallized from alcohol several times with two or three more decolorizations. They were orange crystals with a melting point of 154.5–154.7°.

Preparation of *cis*-4-Nitrostilbene by Illumination.—A method exactly analogous to that used in the preparation of *cis*-4,4′-dinitrostilbene was used: 3.3 grams of *trans*-4-nitrostilbene was illuminated in 200 cc. of 95% alcohol for twenty-three hours. The *trans* compound was recovered upon cooling. More was obtained when the volume of the solution was reduced to half. The *cis* form was brought down by adding water very slowly; too rapid addition causes an emulsion to form. The *cis* was recrystallized from alcohol by water and the crystals were light yellow, m. p. 59–60°. Heating for fifteen minutes at 170° gave the *trans* isomer melting at 152–154°. The yield of *cis* is 0.7 g. or 25%.

Absorption Measurements.—The absorption spectra were obtained photographically on a Hilger quartz prism spectrograph. As a light source the low voltage hydrogen arc of Allen and Franklin[16] was found very satisfactory and Eastman Kodak Co. I-O and III-O plates were used and photometered on a Zeiss microphotometer. The absolute values of the darkening were obtained by use of a set of nine carefully measured screens ranging in transmission from 60% to 1.35%. The absorption cells were of precision highly polished fused quartz supplied by the American Instrument Co. The concentrations of the solutions varied between 10^{-5} and 10^{-3} *M* in absolute alcohol.

Discussion

From the comparison of the spectra in alcohol and acidic alcohol it seems quite certain that at low acidities the salt ion in alcohol solution is mainly in the *cis* form while at high acidities the *trans* form becomes the more stable. It seems quite reasonable to suggest that the two salts are the geometric isomers, although to designate one of them as *cis* and the other as *trans* is not so readily done. By comparison with the results in alcoholic solution one might be inclined to call the red salt the *cis* form since it crystallizes from the solution of lower acidity. On the other hand, all of our experience with the color of *cis* and *trans* isomers of stilbene indicate that the *cis* form should be the lighter in color. Furthermore, the crystallization process cannot be occurring under equilibrium conditions since in that case only one form, whichever is the most stable solid, would precipitate. A phase rule study will be necessary to decide which of these two salts is the most stable form before any assignment of configuration can be attempted.

That the rotation in the free base must be very easy at room temperatures is further borne out by the dipole moment measurements of Hertel and Lührmann.[9] They found the dipole moment of 4-dimethylamino-4′-nitrostilbene in benzene solution to be 7.0 *D*, that of the *trans-p*-nitrostilbene to be 4.9 and that of the *trans-p*-dimethylaminostilbene to be 2.5. Using these as constituent moments we may calculate a lower limit for the *trans* form of 4,4′-dimethylaminonitrostilbene to be 7.4, while that of the *cis* form should be about 5.9. A calculation on the basis of free rotation about the double bond gives the value 7.0. This calculation in itself is not to be taken too seriously but in the light of the data which have been presented it is a bit of additional evidence.

The shifting of the equilibrium toward the *trans* form by the addition of ions can be understood readily when it is assumed that there are two major factors influencing the relative stabilities of *cis* and *trans* isomers of this type, namely, (1) the steric repulsions favoring the *trans* forms, and (2) the coulombic interactions of charges or dipoles favoring the form of lowest dipole moment, which in this case is the *cis* form. The presence of large numbers of ions in the solutions permits a neutralization of the unfavorable charge distribution of the *trans* form and thus permits the steric factors to become predominant and stabilize the *trans* form with respect to the *cis*.

The mechanism of isomerization so far discussed involves the polar breaking of the double bond. Another mechanism is possible, namely, a homopolar break into a diradical form (two unpaired electrons—a triplet state) in the transi-

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(15) Pfeiffer and Sergiewskaja, *Ber.*, **44**, 1109 (1911).

(16) Allen and Franklin, *J. Opt. Soc. Am.*, **29**, 453 (1939).

tion state. This type of mechanism should be favored by the same type of structures which increase the stability of free radicals and experiments are in progress to establish such cases. The catalysis of certain *cis–trans* isomerizations by atoms most probably proceeds by such a mechanism.

Summary

1. It has been shown that the same base is obtained upon half-reduction of both *cis* and *trans* isomers of 4,4′-dinitrostilbene.
2. Two salts of this base have been prepared and it is suggested that they are the geometric isomers of the salts.
3. It has been demonstrated by spectroscopic means that the salts in acidified alcohol exist in both forms in comparatively rapid equilibrium with each other and that this equilibrium can be easily shifted by acid. The *cis–trans* equilibrium is maintained by virtue of the equilibrium between the ion and the base.
4. The significance of the resonance phenomenon in understanding the effects of groups on the ease of rotation about a double bond is indicated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

Iodine Monochloride. III. The Systems Iodine Monochloride–Acetic Acid and Iodine Monochloride–Carbon Tetrachloride[1]

BY JACOB CORNOG AND LEONARD E. OLSON

In an earlier investigation Olson[2] learned that the cryoscopic constant of iodine monochloride decreased from 29 to 3 when the mole per cent. of carbon tetrachloride solute was increased from 0.6 to 23. The freezing point curve based on these data was shaped like the letter "S." Both the abnormally large cryoscopic constants and the rather unusual form of the freezing point curve roused our curiosity and prompted the present study of the cryoscopic preparation of solutions of iodine monochloride. Carbon tetrachloride was chosen as a non-polar, non-reactive solute, and acetic acid as a somewhat polar solute.

The System Iodine Monochloride–Acetic Acid

Materials: Acetic acid of reagent quality was purified by repeated recrystallizations until the freezing point rose to 16.40°.

Iodine monochloride was prepared by the method of Cornog and Karges,[3] and was redistilled in the Cornog and Olson[4] "sublimer." Thus prepared it had a freezing point of 27.3°, which is 0.1° higher than any previously published value.

Procedure.—Glass-stoppered flasks containing mixtures of iodine monochloride and acetic acid were suspended in a thermostat in which the maximum temperature variation was ±0.1°. The temperature of the thermostat and the composition of the mixtures were so regulated that partial freezing occurred. After intervals of from eight to ten days, a pipet was used to remove portions of the liquid phase for analysis. Equilibrium between the solid and liquid phases was assumed to exist when the analyses of successive portions checked within 2%. The temperature of the thermostat was then changed and the routine was repeated. Data thus obtained are shown in Table I and are graphically represented in Fig. 1. The approximate composition and freezing point of the eutectic indicated in Fig. 1 was determined by extending the freezing point curves till they intersected. The location of this eutectic was experimentally verified by determining the freezing point of a mixture having approximately the indicated composition.

TABLE I

COMPOSITION OF THE LIQUID PHASE IN EQUILIBRIUM WITH THE SOLID PHASE

Solid phase–iodine monochloride		Solid phase–acetic acid	
Temp., °C.	Mole per cent.[a] acetic acid	Temp., °C.	Mole per cent.[a] acetic acid
27.3	0.00	16.4	100.0
26.0	4.9	10.2	91.3
25.0	7.3	0.1	82.2
23.0	12.8	−18.2	68.4
20.0	17.8		
19.0	19.6	Eutectic	
17.0	24.0		
15.0	26.7	−35.5	60.0
10.0	34.3		
0.1	42.1		
−18.2	53.2		

[a] Each value in this column represents averages of two or more analyses agreeing within 1.5%.

It can be seen from these data that this system is a simple binary one in which each com-

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[1] This paper is an excerpt from the Ph.D. thesis of Mr. Leonard E. Olson, State University of Iowa (1940).

[2] Olson, unpublished M.S. thesis, University of Iowa (1936).

[3] Cornog and Karges, "Inorganic Syntheses," Vol. 1, p. 165.

[4] Cornog and Olson, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 551 (1939).