method since the error introduced by the liberation of hydrogen on the calculation of the weight of the metal from Faraday's law would be very large.

Summary

A direct method for the determination of the thickness of a surface film of metal, which corrects for the obvious errors of Oberbeck's method, has been devised.

The thickness of a surface film of copper is about 0.39 mμ instead of 0.69–0.73 mμ, as given by Oberbeck.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Kinetics of Thermal Cis–Trans Isomerization. IV

BY G. B. KISTIAKOWSKY AND WALTER R. SMITH

The rates of isomerization of several *cis–trans* isomers in the gas phase have been dealt with in previous contributions.[1] The present paper describes experiments with the methyl esters of the *cis* and *trans* cinnamic acids.

Experimental Details

Preparation of *Cis*-methyl Cinnamate.—Phenylpropiolic acid was prepared by bromination of the ethyl ester of *trans* cinnamic acid and subsequent elimination with alcoholic potassium hydroxide. Treatment with a cold saturated aqueous solution of hydrogen bromide yielded a mixture of β-bromocinnamic and allo-β-bromocinnamic acid.[2] Separation of these two acids was largely effected through the barium salt, the barium salt of the *trans* modification being much less soluble in water than that of the *cis*-β-bromo acid. By treating the acid with zinc dust in alcohol[3] a mixture of about 80% *cis*-cinnamic acid and 20% *trans* cinnamic acid was obtained. A first separation of the acid was carried out by converting the acids to the calcium salts, the salt of the *trans* acid being much less soluble than that of the *cis* form. Final separation was achieved by means of the aniline salt.[4]

Two recrystallizations gave a product melting 82–83°. Treatment with dilute aqueous sodium hydroxide yielded pure isocinnamic acid. The acid was esterified by treating an ether suspension of the silver salt with methyl iodide. The ester was washed with sodium bisulfite, sodium bicarbonate and finally with water. After drying and sucking off all the ether, the ester was twice distilled at reduced pressure; melting point −3.5°; n^{20}_{D} 1.5528.

Preparation of the *Trans* Ester.—The *trans* methyl cinnamate was obtained by treating Kahlbaum cinnamic acid with methyl alcohol in the presence of concentrated sulfuric acid according to the method of Fischer and Speier.[5] The ester had the melting point 34°.

Method of Analysis.—The method of analysis was essentially the same as that described in an earlier paper,[1c] except that the sample was placed in a jacketed tube which was immersed in an unsilvered Dewar flask containing ether chilled to a few degrees below the melting point of the sample. The bath warmed very gradually and the temperature at which the last crystal disappeared was noted by means of a single junction copper–constantan thermocouple. Calibration was effected by following the same procedure with known mixtures of the isomers. Figure 1 is a reproduction of the calibration curve.

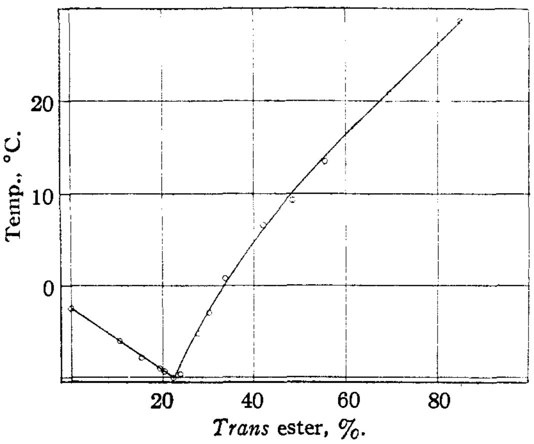

Fig. 1.—Freezing points of *cis* and *trans* methylcinnamic esters.

Experimental Procedure.—The apparatus employed was the low pressure static system described elsewhere.[1b] The technique of starting and stopping runs also has been described adequately in the earlier papers.[1]

Experimental Results and Discussion

The runs with the *cis* isomer proceeded without any appreciable decomposition. On freezing out the product at the end of the run, crystals identical in appearance with the *trans* ester were obtained. Some of the crystals were dried and their melting point determined as 34°, identical with that of the previously prepared *trans* ester. The mixed melting point was unchanged.

Tables I and II present the data accumulated in

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(1) (a) G. B. Kistiakowsky and M. Nelles, *Z. physik. Chem.*, **152**, 369 (1931); (b) M. Nelles and G. B. Kistiakowsky, THIS JOURNAL, **54**, 2208 (1932); (c) G. B. Kistiakowsky and Walter R. Smith, *ibid.*, **56**, 638 (1934).

(2) Sudborough and Thompson, *J. Chem. Soc.*, **83**, 1158 (1903).

(3) Liebermann and Scholz, *Ber.*, **25**, 950 (1892).

(4) Liebermann, *ibid.*, **24**, 1102 (1891).

(5) Fischer and Speier, *ibid.*, **28**, 3254 (1895).

the investigation. Table I shows the effect of pressure on the reaction. It appears that there may be some falling off in the rate at 5 mm. Unfortunately experimental difficulties prevented investigations at still lower pressures. It is also evident that a six-fold increase in the surface available has practically no effect on the rate. The reaction is undoubtedly homogeneous.

TABLE I

T, °K.	p, mm.	Time, sec.	% *trans*	k sec.$^{-1}$ × 10^4
637.5	570	7410	80.6	2.22
635.0	565	3660	59.6	2.48
636.5	308	3210	51.6	2.16
635.5	290	7200	79.2	2.18
637.0	72	2880	48.0	2.27
637	72	4170	60.4	2.22
635[a]	71	2712	43.6	2.11
635.5[a]	68	3600	58.4	2.43
635.5[a]	71	3798	59.4	2.38
634.5[a]	74	5400	66.5	2.03
635.0	5.6	3558	44.5	1.66
635.5	6.8	5730	66.2	1.89
638.0	5.8	7500	76.3	1.92

T = 635 °K. $k_{av.}$[b] = 2.25.

[a] Runs in packed flask 6 × surface. [b] Omitting runs at 6 mm.

Table II demonstrates the temperature dependence of the rate. From the data, represented graphically in Fig. 2, the energy of activation has been determined as 41,600 ± 2000 calories. With this value, the temperature independent factor in the reaction velocity constant is found to be $A = 3.5 \times 10^{10}$.

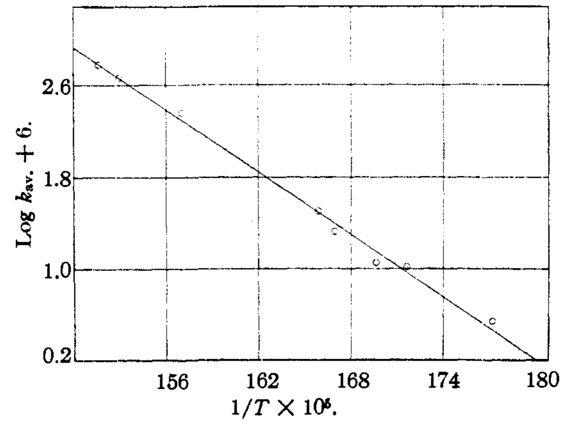

Fig. 2.—Plot of log k against $1/T$.

Methyl cinnamate was chosen for this work primarily because it is, so to speak, a combination of the two compounds previously investigated, methyl maleate and stilbene. The reaction velocity constants of these latter were found to be

$$\text{Maleic ester } k = 6.8 \times 10^5\, e^{-26,600/RT}$$
$$\text{Stilbene } k = 6.0 \times 10^{12}\, e^{-42,800/RT}$$

Comparing these with the new result: $k = 3.5 \times 10^{10}\, e^{-41,600/RT}$, it is immediately obvious that the behavior of cinnamic ester is much closer to that of stilbene than to that of maleic ester. Within experimental error—in the present work it is about 2000 cal.—the activation energies of the stilbene and cinnamate reactions are identical and only the temperature independent factors differ. The latter difference is real, however. It would be necessary to assume

TABLE II

T, °K.	p, mm.	Time, sec.	% *trans*	k sec.$^{-1}$ × 10^4
565	78	54,960	19.0	0.0383
564.5	80	89,580	26.2	.0339
563	80	143,820	35.0	.0300
		T°, $K_{av.}$ = 564.2°	$k_{av.}$ =	.0344
589.5	71	20,880	24.2	0.133
589.5	71	26,430	26.2	.115
590.5	71	31,980	28.3	.104
589.0	71	14,700	14.2	.104
		T°, $K_{av.}$ = 589.8°	$k_{av.}$ =	.114
599.5	73	12,975	23.0	0.202
599.5	69	19,200	34.3	.219
599.0	71	21,840	35.2	.199
598.0	71	43,530	56.6	.192
		T°, $K_{av.}$ = 599°	$k_{av.}$ =	.203
602.5[a]	68	7836	24.4	0.357
601.0[a]	69	10,170	28.0	.323
602.0[a]	71	12,780	30.9	.290
		T°, $K_{av.}$ = 601.8°	$k_{av.}$ =	.323
653.5	71	600	24.7	4.72
653.5	71	1032	34.6	4.34
		T°, $K_{av.}$ = 653.5°	$k_{av.}$ =	4.53
659	77	918	41.0	5.76
660	78	1218	49.9	5.71
660	83	2220	71.3	5.62
		T°, $K_{av.}$ = 659.6°	$k_{av.}$ =	5.70
583	66	17,220	20.9	0.136
584	69	23,460	25.5	.126
583	76	45,240	31.2	.083
583	70	50,280	33.2	.080
		T°, $K_{av.}$ = 583.2°	$k_{av.}$ =	.106
637[a]	72	2880	48.0	2.27
637[a]	72	4170	60.4	2.22
		T°, $K_{av.}$ = 637°	$k_{av.}$ =	2.25

[a] Packed runs 6 × surface.

that the activation reaction of cinnamate is some 48,000 calories—a value quite outside experimental errors—in order to obtain an *A* factor as large as that of stilbene. In line with the smaller *A* factor it is found, of course, that the number of participating internal degrees of freedom is smaller than in the case of stilbene. Carrying out the calculation in much the same manner, assuming the same molecular diameter and a 10% falling off of the velocity constant at 5 mm. pressure, one finds about 6 internal degrees of freedom as against 12 for stilbene. That one number is just one-half of the other is not significant when taking into account all the uncertainties of these calculations. The other results, however, are significant enough to allow some speculations concerning the mechanism of the double bond isomerization. The new results are contributing to the conclusion that there are two such mechanisms. Comparing these results with the maleic ester it appears that the presence of one phenyl group is sufficient to alter the form of the reaction completely; the activation energy is almost doubled, but an easy exchange of internal energy now is taking place. The addition of another phenyl group only further facilitates the energy exchange, not altering the reaction otherwise. This practically eliminates the tentative suggestion made in the preceding paper[1c] that the difference of activation energies of the maleic ester and stilbene reactions is due to a difference in the average internal energy content of these molecules. If that were true, one should have found for cinnamate an activation energy about halfway between those of the other two substances. One is led thus to the conclusion that the reaction in the presence of phenyl groups in the molecule involves in some way a resonance between the double bond and these groups.[6] If the accepted picture of vibrational energy exchange in collisions, as being responsible for unimolecular reactions, is to be retained for the present reaction, one must suppose that the accumulated vibrational energy, in a reversal of the photochemical "predissociation" process, is converted into excitation energy of the electrons forming the double bond. This excitation results then in a loss of rigidity by the double bond, similarly as in the case of photochemical reactions.[7] The function of the phenyl groups is then to provide a suitable electronic state of the molecule, only some 40,000 calories above the normal, having these characteristics and further to supply the vibrational energy necessary for the internal predissociation. The treatment of the reaction as a mechanical rotation around the double bond, not accompanied by electronic excitation, suffers in plausibility from the observation that cinnamate and stilbene have the same activation energies. If the function of the phenyl groups is to stiffen the double bond, 40,000 calories being now necessary to cause free rotation, it is not clear why one group has numerically the same effect as two. The reaction mechanism, thus, must be regarded probably as being essentially different from the mechanical rotation around the double bond, which latter, we believe, is responsible for isomerizations of compounds not containing phenyl groups.

It is noteworthy that the low activation energy reaction if occurring at all with cinnamate is much slower than in the case of maleic acid derivatives. Otherwise it should superimpose itself upon the high activation energy reaction and result—both velocities being comparable at the lower end of the temperature range investigated—in a curved line on a plot of log *k* against inverse this. Further light on this particular question will be thrown, we hope, by experiments now in progress, on the rate of isomerization of *cis* and *trans* butene-2. In this case neither resonance with other double bonds nor enolization is possible.

Summary

1. The rate of isomerization of *cis* methyl cinnamate has been studied at pressures from 500 to 5 mm. and over a temperature range of 563 to 660°K.

2. The reaction appears to be homogeneous.

3. While the rate at 70 to 500 mm. appears to be independent of the pressure, it appears that some falling off may be occurring at 5 mm.

4. The activation energy is computed as 41,600 ± 2000 calories. The rate at the higher pressure is described by: $k = 3.5 \times 10^{10} e^{-41,600/RT}$.

5. The reaction and possible mechanism are discussed in the light of previous work.

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(6) Pauling and Sherman, *J. Chem. Physics*, **1**, 679 (1933).

(7) Olsen, THIS JOURNAL, **55**, 1410 (1933); *ibid.*, **56**, 1320 (1934).