Second, the rate constants for the reaction of the monomethyl esters of these acids with diphenyldiazomethane also differs by less than a factor of 2, while the total variation for the other processes is much larger. Apparently the substitution of a methyl group for one of the carboxyl hydrogens does not materially increase steric hindrance to the reaction with diphenyldiazomethane.

Third, the rate constants for reaction of the *trans*-1,2 forms with diphenyldiazomethane are the greatest, while for the other reactions studied they have been the smallest. Rate constants for reaction of the *cis*-1,2 compounds with diphenyldiazomethane are relatively large. Apparently the electron sink properties of a carboxyl or ester group on another carboxyl group are more important in governing the rate of the reaction than are steric influences. It is also interesting to note that the substituent groups in the *trans*-1,2-acid or ester are presumably in axial positions while for all other forms they are either both equatorial or one equatorial and one axial.[1]

These first three observations are consistent with the mechanism of this reaction as proposed by Roberts and co-workers.[3]

Fourth, if the methyl group of the monomethyl esters exerted no steric or electrical influence, then the reaction rate constants for the diacids should be greater than for the monomethyl esters by a statistical factor of 2. However, these ratios are always less than 2, varying from 1.6 for the *trans*-1,2 forms to 1.9 for the *trans*-1,4 forms. It would thus appear that the acid group in the monoester is more reactive than in the diacid. This apparently indicates that the ester group is a slightly stronger electron sink than the carboxyl group.

Fifth, one notes that for the 1,3- and 1,4-cyclohexanedicarboxylic acids, the *cis*-1,3 and *trans*-1,4 forms behave quite similarly to each other, while the *trans*-1,3 and *cis*-1,4 forms also resemble each other in reaction characteristics. This same result was found for other reactions of the cyclohexanedicarboxylic acids and their esters, and is readily explained on the basis of the conformations of these compounds.[1,2]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Kinetics of the Reaction of Sodium *p*-Toluenethiolate (Alcohol) with Phenylacetylene[1,2]

BY WILLIAM E. TRUCE AND RICHARD F. HEINE

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The kinetics of the reaction of sodium *p*-toluenethiolate with phenylacetylene to produce *cis*-1-phenyl-2-*p*-tolylmercaptoethene have been investigated in absolute ethanol, deuterioethanol and N,N-dimethylformamide–ethanol solvent systems. The results can be interpreted in favor of a concerted mechanism for this addition.

There have been several recent articles concerning the mechanism of vinylation reactions, in particular, concerning the addition of alcoholic alkoxide to an acetylene.[3] The general finding is that the reaction is "pseudo"-first order, that is, first order in acetylene only (since the concentration of alkoxide remains essentially constant during a given run). The fact that no rate dependence on the solvent was observed was interpreted as indicating a mechanism involving initial attack of the alkoxide on acetylene in the slow, rate-determining step, and then a rapid abstraction of a proton from the solvent.

Since we had some reservation about this interpretation and its general applicability, we developed the present rate data concerning the vinylation mechanism, particularly the mechanism of the addition of sodium *p*-toluenethiolate reagent to phenylacetylene, which had previously been shown to be a high-yield stereospecific reaction.[4] This acetylenic compound is a desirable one to use in rate studies involving a thiolate reagent; alkyl acetylenes[4] react too slowly and acetylenes carrying strongly electron-accepting groups react too rapidly at moderate temperatures.

A comparison in deuterioethanol and ethanol solvents was undertaken with the expectation that in a concerted process, with the alcoholic proton (deuteron) involved in the rate-determining step, a rate difference would be observed between the two solvents.

A small rate difference or isotope effect ($k_D/k_H = 1.15$) is indicated by the data (Table I). The significance of this factor will be discussed in following paragraphs.

Rate studies also were made in an "inert," non-proton-donor solvent, containing various amounts of proton donor (ethanol). Of the inert solvents considered, dioxane, diglyme and N,N-dimethylformamide (DMF), the latter was chosen because of its greater solvent power toward the thiolate reagent. The results of these runs (Table II) show the reaction to be much faster in DMF, containing very small amounts of ethanol, than in absolute ethanol. This is contrary to what would normally be predicted on the basis that the rate of a reaction between an ion and a neutral molecule should be faster in the medium which has the lower dielectric constant.[5] Since the dielectric constant

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[1] No. IX in the series, "Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides"; for preceding paper see THIS JOURNAL, **80**, 6450 (1958).

[2] Abstracted from the Ph.D. Thesis of Richard F. Heine, Purdue University, 1957.

[3] (a) R. Rigamonti and L. Bernardi, *Chim. Ind.* (*Milan*), **34**, 561 (1952); *C. A.*, **47**, 2583 (1953); (b) S. I. Miller and G. Shkapenko, THIS JOURNAL, **77**, 5038 (1955); (c) T. Tsurato, *et al.*, *Bull. Chem. Soc. Japan*, **28**, 552 (1955).

[4] W. E. Truce and J. A. Simms, THIS JOURNAL, **78**, 2756 (1956).

[5] (a) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 135 ff.; (b) K. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 130.

TABLE I

COMPARISON OF REACTION RATE IN EtOH *vs.* EtOD

No. of runs	k, l. m.$^{-1}$ sec.$^{-1}$	Solvent
5	$1.5 \times 10^{-5} \pm 0.002 \times 10^{-5}$	EtOH
2	$1.7 \times 10^{-5} \pm 0.002 \times 10^{-5}$	EtOD

TABLE II[a]

RATE IN DMF AS A FUNCTION OF ETHANOL CONCENTRATION

Run	Mole fraction,[b] EtOH	k, l. m.$^{-1}$ sec.$^{-1}$[c]
10	0.103	2.35×10^{-4}
11	.103	
12	.103	
13	.200	1.6×10^{-4}
14	.294	1.3×10^{-4}
15	.384	1.0×10^{-4}
16	.649	4.5×10^{-5}
17	1.000	1.5×10^{-5}

[a] Temperature 59.20 ± 0.02°. [b] Several runs at 0.0 mole fraction ethanol were inconsistent and possibly were affected by small amounts of moisture entering the system when samples were taken. However, the data do suggest that the reaction is slower in DMF alone than when a small amount of ethanol is present. This may be due to the reaction being reversible if it cannot go immediately to completion. [c] The probable error in these values is $\pm 0.67 \times 10^{-5}$.

of ethanol is 25.1 and of DMF is 37.6,[6] one would expect the reaction to be faster in ethanol than in DMF. Inasmuch as the reverse is true and assuming the charge becomes more diffuse in the transition state, then an additional factor must be involved. A clue to its nature is offered by the thermodynamic data of the reaction (Table IV), which were calculated from the rate data for two different temperatures (Table III).

TABLE III

RATE AS A FUNCTION OF TEMPERATURE

Run	Temp., °C.	k, l. m.$^{-1}$ sec.$^{-1}$
A.	DMF solvent containing 1.365 moles/l. EtOH	
1–3	39.20 ± 0.02	
		Av. $3.52 \times 10^{-5} \pm 0.067 \times 10^{-5}$
4–6	59.20 ± 0.02	
		Av. $2.35 \times 10^{-4} \pm 0.067 \times 10^{-4}$
	B. Ethanol solvent	
7–9	39.20 ± 0.02	
		Av. $3.22 \times 10^{-6} \pm 0.25 \times 10^{-6}$
10	59.20 ± 0.02	Av. of 9 runs $1.48 \times 10^{-5} \pm 0.033 \times 10^{-5}$

Table IV indicates that the reaction has a higher energy of activation in the solvent in which it is faster, a not uncommon phenomenon.[5] Also, not uncommonly, it is to be noted that the faster reaction has a much lower entropy loss than the slower reaction. Assuming the validity of these results, there appear to be at least three possible explanations for these rate and thermodynamic data: (1) The difference in the degree of solvation of the activated complex as compared to the reactants may change appreciably from one solvent to the other. (2) There may be two competing mechanisms. (3) There may be a change in mechanism in going from one solvent to the other.

TABLE IV

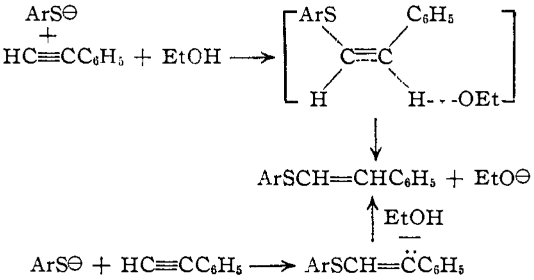
VARIATION IN ΔH^* AND ΔS^* WITH SOLVENT

k, l. m.$^{-1}$ sec.$^{-1}$	Temp., °C.	ΔH^{+}, kcal./mole	ΔS^*, e.u.	Solvent
2.35×10^{-4}	59.20 ± 0.02	18.8 ± 0.5	-10.3 ± 2	DMF[a]
1.48×10^{-5}	59.20 ± 0.02	14.2 ± 0.5	-30.0 ± 2	EtOH

[a] Containing 1.365 moles/l. ethanol.

The first explanation requires that the increase in the solvation of the activated complex as compared to the reactants be greater in ethanol than in DMF in order to explain the difference in ΔS^*'s. Although, generally speaking, the activated complex is considered to be somewhat more solvated than the reactants in a reaction between an ion and a polar, but neutral, molecule,[5a] the greater difference should be observed in the solvent with the greatest solvating ability, in this case DMF. This would lead to a contradiction of results, unless H-bonding of the activated complex were assumed, which is a possibility, since ethanol would more readily H-bond than DMF. This latter possibility would make ΔH^* lower in ethanol than in DMF and of course account for the larger negative ΔS^* in ethanol than in DMF. On these assumptions, then, we could account for the data obtained in terms of a stepwise process.

The second and somewhat more appealing explanation considers that there may be two competing mechanisms, one being favored in ethanol and another in DMF, with a varied amount of each occurring in mixtures of the two solvents. The two competing mechanisms could be a concerted and a stepwise mechanism, *e.g.*, equations 1 and 2, respectively, with (1) having predominance in ethanol and (2) in DMF.



(1)

(2)

This would seem to be a very logical explanation since a termolecular, concerted mechanism would be expected to exhibit a larger negative entropy of activation than a simpler bimolecular mechanism. Also the effect of ethanol and thus available proton concentration could be expected to bring about this mechanism shift.

The normally low probability of a termolecular process would not be significant here since, in ethanol, the acetylene would have available to it an abundance of ethanol molecules for essentially simultaneous donation of a proton for every reaction with thiolate. The availability of ethanol to the activated complex makes the concerted process quite appealing when the reaction is run in ethanol. However, in DMF with only a small amount of proton donor available the probability of a concerted mechanism would be reduced considerably and the reaction can assume an essentially bimolecular mechanism, followed by a rapid abstraction of a proton from the ethanol.

(6) G. R. Leader and J. F. Gormley, THIS JOURNAL, **73**, 5731 (1951).

The small but definite isotope effect in deuterioethanol would be in agreement with a concerted process occurring in ethanol. The reactions most closely related to ours as regards the role of the proton or deuteron are some neutralizations of carbanions, where the rate-determining step is presumably a nucleophilic displacement of ethoxide by the carbanion on hydrogen (deuterium). In several such reactions, a small inverse effect has been reported ranging from 1.03 to 1.19.[7] This is consistent with the small isotope effect in our study, where solvent would play a like role in the rate-determining step, *i.e.*, abstraction of a proton or deuteron from the solvent by the "developing carbanion."

This speculative interpretation is not readily reconciled with the results of prior studies.[3] The nature of the system involved may be a basis for the difference; also, the temperature difference might be a contributing factor, since it might be expected that solvation would be inversely proportional to temperature.

Experimental

Preparation of Ethanol-*d*.—The ethanol-*d* was prepared by heating a mixture of 25 g. (1.25 moles) of 99.5% deuterium oxide with 180 g. (1.11 moles) of aluminum ethoxide[8] for two hours at 50° after the initial exothermic reaction had subsided[9]; weight 61.0 g. (1.11 moles), b.p. 78.5–79.0°, $n^{18.5}\text{D}$ 1.3613. A comparison of the peak at 2.73 μ in its infrared spectrum with the corresponding peak in absolute ethanol indicated the presence of about 12% ethanol.

Reagent Solutions for the Kinetics Run and Method of Analysis.—Standard sodium hydroxide and hydrochloric acid solutions were each about 0.1 *N*. Sodium mercuric iodide reagent was made up from 250 ml. of a 20% aqueous solution of sodium iodide and 50 g. of mercuric iodide.

The method of analysis is that of Hanna and Siggia.[10] In carrying out the sampling, a 2-ml. aliquot was removed from the reaction mixture and delivered into an aqueous methanolic solution of an excess of sodium mercuric iodide reagent. A known amount of excess base was added to this mixture and the flask was shaken briefly, then titrated to a phenolphthalein end-point with standard hydrochloric acid. Since the reagent reacts quantitatively with both the thiol and the acetylene, the amount of unreacted acetylene plus thiol was obtained. Previous work[4] had shown that only a monoadduct was formed in the reaction; therefore the assumption was made that the thiol and phenylacetylene reacted in a 1:1 ratio.

When the data obtained in this manner were plotted as a function of either

$$\frac{2.3}{a-b}\log\frac{a}{b}\frac{b-x}{a-x} \text{ or } \frac{x}{a(a-x)}$$

(depending on whether or not a and b were in equal concentration) *versus* t, a straight line was obtained, which is indicative of a second-order reaction.[5] The data did not fit either a third- or first-order plot.

The values of ΔH^* of Table IV were obtained from a plot of $1/T$ *vs.* $\log k$; ΔS^* was evaluated from the equation[5]

$$k = \frac{KT}{h}e^{-\Delta H^*/RT}e^{\Delta S^*/R}$$

Procedure and Preparation of Materials for Rate Determinations.—The *p*-toluenethiol (Eastman Kodak Co.) was used directly as obtained. Analysis did not detect any disulfide impurity. In some runs the thiol was converted to sodium *p*-toluenethiolate by adding a slight excess of the thiol to refluxing toluene containing sodium. The mixture was stirred vigorously until all the sodium had reacted (2–3 hr.), then filtered rapidly with suction and stored in a vacuum desiccator over phosphorus pentoxide.

The phenylacetylene (Eastman Kodak Co.) was redistilled and the fraction boiling at 52–54° (29 mm.) was used throughout. Occasionally it was necessary to redistil this material, although storage in a refrigerator avoided deterioration for considerable lengths of time.

The DMF used in this work was dried over calcium hydride for a week or longer, then filtered, distilled (b.p. 152°) and stored in a tightly-stoppered bottle until used.

The most satisfactory procedure for the rate runs was to dissolve a weighed amount of sodium *p*-toluenethiolate in the solvent in a 25-ml. volumetric flask and add a specified amount of phenylacetylene. The contents were diluted with more solvent to within 1% of the desired volume, 25 ml. When DMF was the solvent, the reactants were dissolved in DMF, ethanol was added and the mixture then diluted to the desired volume with DMF. Zero time was the time of immersion in the constant-temperature bath, the maximum error in time being not more than 2 minutes, and usually less than 1 minute.

Blank runs were made on phenylacetylene in sodium ethoxide solution and on sodium *p*-toluenethiolate in ethanol and DMF, all at 59.20 ± 0.02°. In ethanolic sodium ethoxide, phenylacetylene showed a rate constant for its disappearance of less than 1.7×10^{-8} l.m.$^{-1}$sec.$^{-1}$, or less than 1/100 that for the thiolate-phenylacetylene reaction. In ethanol, sodium *p*-toluenethiolate, at 59.2°, did not exhibit any reaction after 24 hr., although in DMF a slow reaction was observed with an estimated *k*-value of 3.3×10^{-9} l.m.$^{-1}$sec.$^{-1}$ at 39.2°. This again is too small to affect the results.

The product isolated from runs in each solvent was identical with authentic *cis*-1-*p*-tolylmercapto-2-phenylethene as indicated by mixed melting point determinations.

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[7] K. B. Wiberg, *Chem. Revs.*, **55**, 723 (1955). It is interesting to note that either small inverse or large normal isotope effects seem to be observed.

[8] W. Chalmers in A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 599.

[9] S. J. Cristol and D. D. Fix, THIS JOURNAL, **75**, 2645 (1953).

[10] J. G. Hanna and S. Siggia, *Anal. Chem.*, **21**, 1469 (1949).