[CONTRIBUTION FROM THE RUBBER RESEARCH LABORATORY OF THE UNIVERSITY OF AKRON]

Kinetics of Bisulfite Addition to α,β-Unsaturated Compounds[1,2]

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The kinetics of the addition of bisulfite in aqueous solution to acrylonitrile, methacrylonitrile, methyl acrylate and methyl methacrylate were studied. The reactions were found to be second order over a range of concentrations from 0.01 to 0.10 *M*, at *p*H values ranging from 4 to 8. Increase in *p*H resulted in a marked increase in reaction rates, in a manner which indicated that the sulfite ion concentration controlled the rate of the reaction. On this basis, the following rate constants were obtained for three of the compounds investigated: methyl acrylate, $k_1 = 2.0 \times 10^8 \exp(-12000/RT)$ l./mole/sec.; methyl methacrylate, $k_1 = 1.1(\pm 0.3) \times 10^6 \exp(-12000/RT)$l./mole/sec.; methacrylonitrile, $k_1 = 4.0\ (\pm 1.3) \times 10^9 \exp(-18000/RT)$l./mole/sec. An anomalous trend was obtained in the activation energy of the fourth compound, acrylonitrile.

Introduction

It is well known that bisulfite salts add readily to aldehydes and ketones, but only with great difficulty to ordinary ethylenic linkages. However, this addition reaction apparently occurs quite readily at the ethylenic bond in α,β-unsaturated compounds such as aldehydes, ketones, acids and esters.

The present work arises from a polymerization study of water-soluble monomers, such as methyl methacrylate and acrylonitrile, in aqueous solution. In polymerizations of this type the bisulfite ion apparently has a catalytic effect in the presence of oxidizing agents. Since monomers of this type are capable of adding bisulfite, the rate of polymerization is sensitive to conditions which may affect the extent of such a side reaction. This study was undertaken to throw some light on the mechanism of this addition reaction, which has received only scant mention in the literature.

No actual rate studies have been reported for the addition of bisulfite to α,β-unsaturated systems. Stewart and Donnally[3] observed that the rate of decomposition of the bisulfite–aldehyde product increased with lower *p*H (down to 1.8) and then decreased again. On the basis of the two ionization constants of sulfurous acid, they concluded that in the *p*H range of 3 to 13 this reaction involves the sulfite ion rather than the bisulfite ion. Bacon[4] observed an exothermic reaction between acrylonitrile and sodium sulfite, accompanied by a rise in *p*H, according to the equation

$$\mathrm{CH_2{=}CHCN + Na_2SO_3 + H_2O \longrightarrow CH_2SO_3CH_2CN + NaOH}$$

The kinetic study of Gubarova[5] on the bisulfite addition to acetone has shown that the rate decreases with a decrease in *p*H. The activation energy for this reaction was found to be 6 to 8 kcal.

In the present work some preliminary experiments showed that sodium sulfite or bisulfite added very rapidly and quantitatively to such compounds as acrylonitrile or methyl acrylate in aqueous solution, even at concentrations of 0.01 *M*. Furthermore the rate of the reaction was very sensitive to *p*H and unaffected by the presence of a free radical inhibitor such as hydroquinone. Hence an ionic mechanism is indicated. Since free hydroxyl ions are released by this reaction, an adequate hydrogen ion buffer system is required for any kinetic study.

The four compounds studied were acrylonitrile, methacrylonitrile, methyl acrylate and methyl methacrylate. The study comprised an investigation of the effect of *p*H and concentration on the order of the reaction, as well as an evaluation of the activation energy.

Experimental

A. Materials Used.—The following materials were used: Acrylonitrile, technical grade (American Cyanamid Company). This was freed from inhibitor by washing with a 1% sodium hydroxide solution and then vacuum distilled at 30° under nitrogen. The *p*H of a 1% aqueous solution of acrylonitrile was 6.5 after washing, as compared with a *p*H of 9 originally.

Methacrylonitrile was received from the Shell Development Company. This methacrylonitrile was inhibited with 0.05% *p*-*t*-butylcatechol. To remove the inhibitor, the material was washed first with a sodium hydroxide–sodium chloride solution, then washed with a saturated sodium chloride–water solution, dried and vacuum distilled at 70° under nitrogen.

Methyl acrylate was received from Rohm and Haas and contained 0.25% hydroquinone. The sample was purified in the same manner as the methacrylonitrile.

Methyl methacrylate was received from Rohm and Haas and contained 0.006% hydroquinone. The same method was used for purifying as in the case of the methacrylonitrile with the exception that before vacuum distilling at 85° the methyl methacrylate was left overnight in calcium sulfate and then filtered.

The water was boiled about 15 minutes to remove most of the dissolved oxygen and then cooled under a stream of nitrogen (Linde high purity). The water was stored under nitrogen.

Sodium sulfite used was Merck Analytical reagent grade (anhydrous).

Iodine Solution.—A 0.01 *M* iodine solution was used containing 0.02 *M* potassium iodide and consisting of 40% by volume of ethanol. The iodine was Merck reagent grade and the potassium iodide was C.P. Baker analyzed.

Buffer Systems.—The *p*H of the system was adjusted by means of the following two buffer systems, which were capable of maintaining the required *p*H values (±0.1 unit) during the course of the reaction, in the presence of the reactants at the concentrations used.

*p*H	Acetate buffer acetic acid, *M*	Sodium acetate, *M*
6	0.025	0.470
5	.033	.060
4	.073	.006

*p*H	Phosphate buffer Na_2HPO_4, *M*	H_3PO_4, *M*
8	0.113	0.0092
7	.113	.080
6	.113	.312

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(1) Presented at the 119th Meeting of the American Chemical Society in Cleveland, Ohio, April, 1951.

(2) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the U. S. Government Synthetic Rubber Program.

(3) T. D. Stewart and L. H. Donnally, THIS JOURNAL, **54**, 2333, 3559 (1932).

(4) R. G. R. Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946).

(5) M. A. Gubarova, *J. Gen. Chem.* (*U.S.S.R.*), **18**, 238 (1948).

B. Procedure.—The reactions were carried out in 500-ml. volumetric flasks under an atmosphere of Linde high-purity nitrogen, the flasks being immersed in a water-bath and thermostated at the desired temperature (±0.05°) without any agitation.

The following general method of charging the flasks was used: (a) The unsaturated compound was dissolved in water. (b) Buffer system was then added. (c) Sodium sulfite solution was added last and flasks were made up to correct volume with water. The reaction time was measured upon the addition of the sodium sulfite solution. At various intervals, samples of 25 to 50 ml. were removed and the bisulfite analysis was carried out by iodimetric titration using the 0.01 *M* iodine solution and starch indicator.

The titration was generally conducted by running the bisulfite solution into a known quantity of iodine solution as rapidly as possible, to avoid air oxidation of the bisulfite.

For a range of *p*H values from 6 to 8, a phosphate buffer was used as the acetic–acetate system did not work in this range. This system was only used to study the addition reactions between 0.05 *M* methyl methacrylate and sulfite.

Effect of *p*H and Concentration on Reaction Order.—In Fig. 1, is shown the effect of *p*H on reaction rate between sodium sulfite and methyl acrylate (0.01 *M* reactants). It can be seen that the rate increases markedly with increase in *p*H.

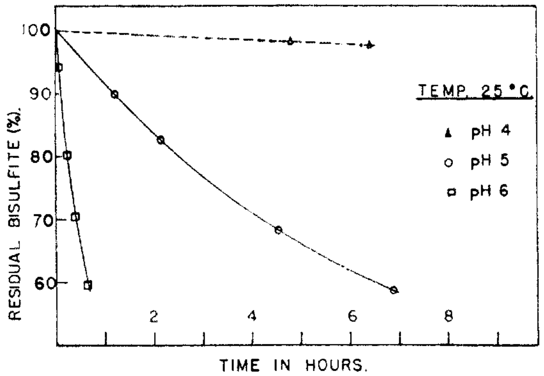

Fig. 1.—Effect of *p*H on rate of methyl acrylate–bisulfite addition.

The methyl acrylate rate curve shows that a *p*H of 5 gives a suitable rate for measurement. Similar rate curves were also found for acrylonitrile. Hence, the rates for both of these compounds were measured at a *p*H of 5 using acetate buffer. These rates can be plotted on a bimolecular scale, as shown in Figs. 2 and 3.

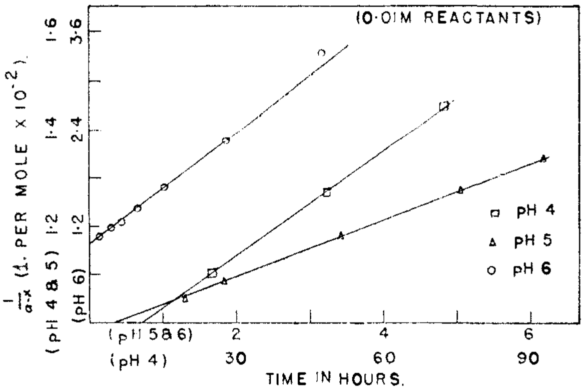

Fig. 2.—Typical bimolecular plot bisulfite–acrylonitrile reaction at 25°.

The reaction seems to be second order over a large extent of reaction and over the whole *p*H range studied. The bimolecular rate constant for the methyl acrylate reaction is approximately twice that found for acrylonitrile at a *p*H of 5.

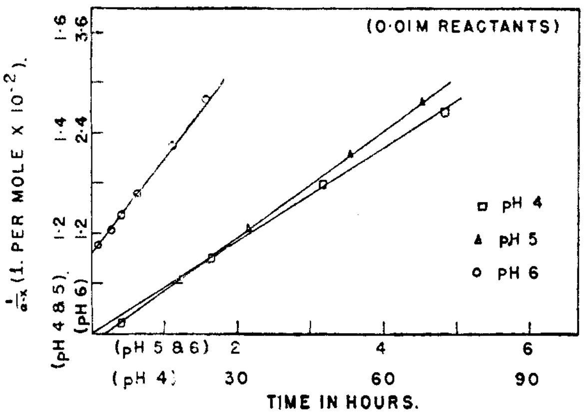

Fig. 3.—Typical bimolecular plot bisulfite–methyl acrylate reaction at 25°.

Changing the initial concentration of the reactants from 0.01 to 0.10 does not affect the order of the reaction as is shown by Figs. 4 and 5, both for equal and unequal concentrations. Thus the bisulfite–acrylonitrile reaction (at 25° in an acetate buffer at *p*H 5) gives an apparent value of 1.30×10^{-3} liter/mole/sec. for the rate constant with equimolecular concentrations and an apparent value of 1.20×10^{-3} liter/mole/sec. for unequal concentrations of reactants.

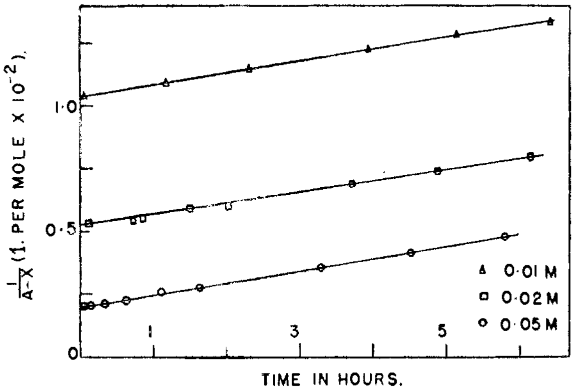

Fig. 4.—Second-order plot bisulfite–acrylonitrile reaction at 25°—*p*H 5 (equimolar concentrations).

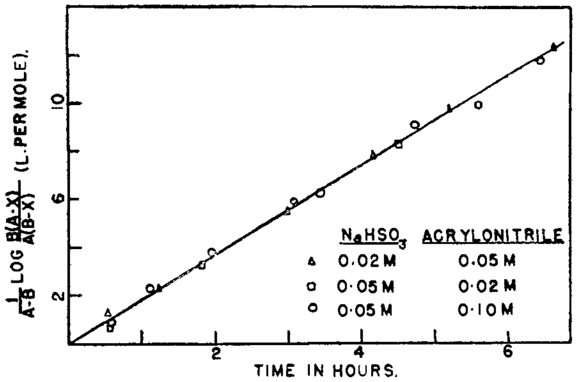

Fig. 5.—Second-order plot bisulfite–acrylonitrile reaction at 25°—*p*H 5 (unequal concentrations).

Since the apparent rate constants show excellent agreement over varied concentrations at the same *p*H, it would appear that the *p*H affects the rate constant by changing the concentration of one of the ions involved. The rate constants appear to be inversely proportional to the hydrogen ion concentration, which indicates that the rate-governing step in this type of reaction seems to be the addition of sulfite ion.

The two ionization constants of sulfurous acid are most reliably reported[6] to be as follows: first ionization constant, 1.72×10^{-2}; second ionization constant, 6.24×10^{-8}.

The first ionization constant would not be involved in the *p*H range studied, but the second ionization constant must be considered. In order to confirm the effect of this ionization constant, the *p*H range was extended up to a value of 8 for methyl methacrylate, since the reaction rate was slow enough to be studied in that case. For the *p*H range of 6 to 8 the phosphate buffer system was used, since the acetate buffer system could not maintain a constant *p*H in this region. The rate of the reaction between sulfite and methyl methacrylate (0.05 *M* reactants) is shown in Fig. 6 as a bimolecular plot, including the acetate buffer system at *p*H 6 for comparison. Again a second-order reaction rate is indicated although only up to the first 40% of the reaction interval, after which the rate falls off. It should be mentioned here that although both *p*H 6 buffers were adequate in maintaining a constant *p*H throughout the reaction, this was not the case at higher *p*H values. Thus at a *p*H of 7 there was no change during the first 40% of the reaction but the *p*H rose to 7.5 after 55%. The *p*H 8 buffer system was not very effective since the *p*H slowly increased to a value of 9.9 after 30% of the reaction. However, on the basis of the second ionization constant of sulfurous acid, the effect of *p*H on the rate is quite small above a *p*H of 7, hence lack of buffering power would not be serious. At any rate, this cannot account for the decrease in rates noted in the later stages of the reaction.

Using the linear slopes obtained during the first part of the reaction, it is possible to calculate a bimolecular rate constant for the reaction between methyl methacrylate and sulfite ion. Since the ionic strength of the solutions used is fairly high, it is important to consider the secondary salt effect. Fortunately, the work of Tartar and Garretson[6] includes data on the variation of the ionization constant with ionic strength, from which it is possible to extrapolate to the values of ionic strength encountered here. Table I shows the calculated rate constants for the methyl methacrylate sulfite reaction at 25°, based on the second ionization constant of sulfuous acid. The apparent rate constants are included for comparison.

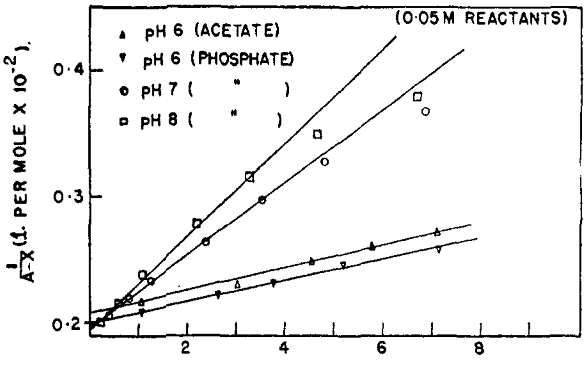

Fig. 6.—Effect of *p*H on rate of sulfite-methyl methacrylate addition at 25°.

TABLE I

CALCULATED RATE CONSTANTS FOR ADDITION OF SULFITE ION TO METHYL METHACRYLATE IN PHOSPHATE BUFFER

*p*H	Initial concn. of reactants, 0.05*M* $K_2 \times 10^7$	Rate constant (l./mole/sec. $\times 10^3$) Apparent	Calcd.
6 (acetate)	3.0	0.28	1.21
6	2.5	0.23	1.15
7	2.5	0.81	1.13
8	3.0	1.03	1.06

It is obvious that the values thus obtained for the rate constants are in sufficiently good agreement to indicate that the addition of the sulfite ion is indeed the rate-governing step in this reaction. On this basis, rate constants were calculated for the reactions of all the other compounds studied, and are shown in Table II.

In the case of acrylonitrile and methyl acrylate, the values for the rate constant show reasonably good agreement at different values of concentration and *p*H. However, in the case of the methyl methacrylate, a concentration effect is noticeable. In a later section, it will be seen that there is also a concentration effect observable for methacrylonitrile. It should be noted that these two compounds show a much lower rate constant for this reaction, hence the rates had to be studied at higher values of concentration and *p*H.

TABLE II

CALCULATED RATE CONSTANTS FOR ADDITION OF SULFITE ION AT 25° IN ACETATE BUFFER

Compound	*p*H	Concn. of reactants (*M*)	$K_2 \times 10^7$	*k* (l./mole/sec.) $\times 10^2$
Acrylonitrile	4	0.01	0.8	22
	5	.01	.9	16
	5	.02	.9	13
	5	.05	.9	15
	6	.01	1.3	18
Methyl acrylate	4	0.01	0.8	21
	5	.01	.9	33
	5	.02	.9	33
	5	.05	.9	31
	6	.01	1.3	29
Methacrylonitrile	6	0.10	3.0	0.035
Methyl methacrylate	6	.05	3.0	.13
	6	.10	3.0	.23

Effect of Temperature.—In Tables III and IV are shown values for the activation energy obtained from the temperature coefficient of the rate constant. For acrylonitrile and methylacrylate, the average value of the rate constant obtained at any given temperature was used, since no concentration effect was present. However, for meth-

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[6] H. V. Tartar and H. H. Garretson, THIS JOURNAL, **63**, 808 (1941).

acrylonitrile and methyl methacrylate, the rate constants at different temperatures were compared at similar concentrations only, as shown in Table IV.

TABLE III

ACTIVATION ENERGY FOR ADDITION OF SULFITE ION TO ACRYLONITRILE AND METHYL ACRYLATE (pH 5)

$T_2 - T_1$(°K.)	$k_2 - k_1$ (l./mole/sec. × 10^2)	Activation energy (kcal./mole)
	Acrylonitrile	
298 − 288	14 − 4.9	18.0
308 − 298	32 − 14	15.3
318 − 308	49 − 32	8.2
	Methyl acrylate	
308 − 298	66 − 33	12.7
318 − 308	116 − 66	11.1

TABLE IV

ACTIVATION ENERGY FOR ADDITION OF SULFITE ION TO METHYL METHACRYLATE AND METHACRYLONITRILE (pH 6)

$T_2 - T_1$ (°K.)	Concn. (M)	$k_2 - k_1$ (l./mole/sec.)	Activation energy (kcal./mole)
		Methyl Methacrylate	
308 − 298	0.05	0.26 − 0.12	12.4
308 − 298	.10	.45 − .22	12.8
318 − 308	.05	.51 − .26	13.5
318 − 308	.10	.79 − .45	11.1
		Methacrylonitrile	
308 − 298	0.10	0.087 − 0.035	16.2
318 − 308	.05	.14 − .046	21.2
318 − 308	.10	.23 − .087	18.6
328 − 318	.02	.47 − .20	17.4
328 − 318	.05	.28 − .14	15.0
328 − 318	.10	.69 − .23	23.1

It can be seen that the activation energy values obtained with acrylonitrile show a progressive decrease with higher temperature. This is difficult to explain and seems to occur only in this one case. It may be due to a change in mechanism, or may be related to the tendency of this compound to show hydrogen bonding, which would lead to association at lower temperatures thus reducing the activity. The energy values for the other three compounds are fairly consistent, the methacrylonitrile showing some spread in values.

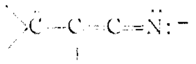
On the basis that the sulfite ion concentration is the rate-governing factor, the following rate expressions may be written for the three compounds listed, omitting the acrylonitrile because of the dubious values for the activation energy

Compound	Rate constant (l./mole/sec.)
Methyl acrylate	$2.0 \times 10^8 \exp(-12000/RT)$
Methyl methacrylate	$1.1(\pm 0.3) \times 10^6 \exp(-18000/RT)$
Methacrylonitrile	$4.0(\pm 1.3) \times 10^9 \exp(-18000/RT)$

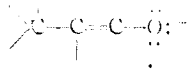
It is apparent that the two acrylates show a much lower activation energy than the nitrile, while the latter has the lowest steric factor. Substitution of the hydrogen by a methyl group increases the steric factor by about 100, while substitution of the nitrile group by a carbomethoxy group increases the steric factor by about 10^3.

The higher activation energy of the nitrile might seem surprising at first glance since a nitrile group would be expected to exert a greater inductive effect on the electrons than the less electronegative carbomethoxy group. However, in these α,β-unsaturated systems, the resonance effect can be expected to predominate, leading to the polarized forms

nitrile



acrylate



Hence it might be expected that the resonance polarization would be more powerful for the acrylate due to the more electronegative character of the oxygen as compared to the nitrogen atom.

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