

# Addition of Hydrogen Sulfite to Bicyclo[2.2.1]heptenes. I. Kinetics of Some 2-Norbornenols and 2-Norbornenylmethanols in Aqueous Sodium Hydrogen Sulfite Solutions

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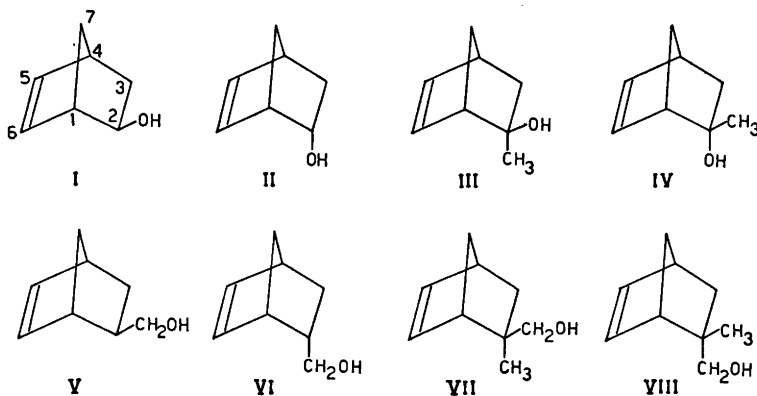
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Addition rates of sodium hydrogen sulfite to the double bond of some 2-norbornenols and 2-norbornenylmethanols measured in aqueous solutions at pH 5.0 were observed to be surprisingly high for olefins having no carbonyl or cyano groups conjugated with the ethylenic linkage (half-lives were from 14 to 140 min at 25 °C when  $[\text{HSO}_3^-]_0 = [\text{olefin}]_0 = 0.01 \text{ M}$ ). The apparent second- and third-order rate coefficients were measured and corresponding activation parameters calculated. The order of the reaction was concluded to be between two and three, and an oxygen-initiated free-radical mechanism, which is in agreement with the formal kinetics, was proposed.

It has been known for a long time that sodium hydrogen sulfite easily reacts with oxygen-carbon double bonds, if they are not sterically hindered, and it also adds fairly easily to carbon-carbon double bonds conjugated with carbonyl or cyano groups, but ordinary ethylenic double bonds have generally been found

to react with hydrogen sulfite slowly.<sup>1-10</sup> However, some 2-norbornenols and 2-norbornenylmethanols, dissolved in ether, were recently found to disappear quite rapidly when they were shaken with one molar aqueous hydrogen sulfite.<sup>11</sup> The addition probably takes place *via* a free-radical mechanism, since a free-radical inhibitor, such as hydroquinone, prevents it from occurring.<sup>11</sup> Hence the mechanism differs from the usual ionic addition reactions which occur at the ethylenic linkage of  $\alpha,\beta$ -unsaturated aldehydes, ketones, acids, esters, and nitriles.<sup>1-8</sup>

In this work the rates of addition of sodium hydrogen sulfite to four 2-norbornenols [*exo*-2-norbornenol (I), *endo*-2-norbornenol (II), 2-methyl-*exo*-2-norbornenol (III), and 2-methyl-*endo*-2-norbornenol (IV)] and to four 2-norbornenylmethanols [*exo*-2-norbornenylmethanol (V), *endo*-2-norbornenylmethanol (VI), 2-methyl-



yl-*exo*-2-norbornenylmethanol (VII), and 2-methyl-*endo*-2-norbornenylmethanol (VIII)] were measured under homogeneous conditions at varying temperatures and in one case (IV) by changing systematically the concentration of hydrogen sulfite.

EXPERIMENTAL

*Preparations.* The syntheses of the substrates I and II,<sup>12</sup> III and IV,<sup>13,14</sup> as well as V, VI, VII, and VIII,<sup>15</sup> have been described earlier. The purities were measured by gas chromatography (FFAP and Carbowax 1500 columns) and found to be ≥ 99 % for I, II, IV, VI, and VII, 97 % (3 % of IV) for III, and 95 % (5 % of VI and VII, respectively) for V and VIII. The saturated alcohols, which were used as inert internal standards in GLC analyses of the kinetic runs, were prepared as follows. *exo*-2-Norborneol was obtained by hydrolyzing the *exo* formate formed by addition of formic acid to norbornene.<sup>16</sup> 2-Norbornylmethanol (*exo:endo* = 1:2, the isomers gave a common peak in GLC) was obtained by catalytic hydrogenation of a mixture of 2-norbornenylmethanols. The synthesis of 3-nortricyclanol has been reported earlier.<sup>12</sup> The purities of the internal standards were ≥ 99 %.

*Kinetic measurements.* The reaction medium consisted of 20 cm<sup>3</sup> of an acetic acid-0.2 M sodium acetate buffer solution of pH 5.0 and of such amounts of 0.2 M sodium chloride and 0.2 M hydrogen sulfite solutions that the total volume was 40 cm<sup>3</sup>. (The concentration of HSO<sub>3</sub><sup>-</sup> is at its maximum at pH 4.4 and [SO<sub>3</sub><sup>2-</sup>] ≤ 0.01 [HSO<sub>3</sub><sup>-</sup>] at pH 5.0.<sup>17</sup>) The water used for reaction media was saturated with air. The ionic strength of the medium was 0.20 M and the hydrogen sulfite concentration was usually from 0.009 to 0.014 M. The kinetic measurements were carried out under similar exposure to light. The internal standard (0.003–0.005 M) was added into the thermostated medium and the reaction was started by adding the substrate (0.003–0.009 M) as neat or as dissolved in 1 cm<sup>3</sup> of purified<sup>18</sup> dioxane. Samples of 2 cm<sup>3</sup> (10–12 in numbers) were rapidly transferred into a separatory funnel, which contained 5 cm<sup>3</sup> of heptane. After shaking the organic phase was separated and analyzed by GLC. The heights of the peaks (*h*) of the substrate and the internal standard were measured from chromatograms (2–5 measurements per sample) and their ratios were calculated ( $r = h_{\text{substrate}}/h_{\text{standard}}$ ).

The ratio calculated for the first sample ( $r_0$ ) taken shortly after the initiation of the reaction was preliminarily fixed to correspond to the initial substrate concentration ([ROH]<sub>0</sub>). The substrate and hydrogen sulfite concentrations ([ROH]<sub>*t*</sub> and [HSO<sub>3</sub><sup>-</sup>]<sub>*t*</sub>) of samples taken

after time *t* had elapsed from removal of the first sample are given by:

$$[\text{ROH}]_t = \frac{r_t}{r_0} [\text{ROH}]_0 \tag{1}$$

$$[\text{HSO}_3^-]_t = [\text{HSO}_3^-]_0 - ([\text{ROH}]_0 - [\text{ROH}]_t) \tag{2}$$

The second-order rate coefficient was calculated from the equation

$$k_2 t = \frac{1}{[\text{HSO}_3^-]_0 - [\text{ROH}]_0} \ln \frac{[\text{ROH}]_0 [\text{HSO}_3^-]_t}{[\text{HSO}_3^-]_0 [\text{ROH}]_t} \tag{3}$$

In all cases the substrate disappeared totally giving zero value for the final concentration.

The corrected initial ratio for the substrate was calculated from the equation

$$r_0 = r_0' (1 + [\text{HSO}_3^-]_0 \Delta t k_2) \tag{4}$$

where  $\Delta t$  is the time elapsed from the addition of the substrate into the flask ( $r = r_0$ ) to taking the first sample ( $r = r_0'$ ). The corrected rate coefficients were calculated from eqns. (1)–(3) by replacing  $r_0'$  by  $r_0$  and *t* by *t* +  $\Delta t$ .

The third-order rate coefficient was calculated from the equation

$$(t + \Delta t) k_3 = \frac{1}{([\text{HSO}_3^-]_0 - [\text{ROH}]_0)^2} \ln \frac{[\text{ROH}]_0 [\text{HSO}_3^-]_t}{[\text{HSO}_3^-]_0 [\text{ROH}]_t} + \frac{1}{[\text{HSO}_3^-]_0 - [\text{ROH}]_0} \left( \frac{1}{[\text{HSO}_3^-]_0} - \frac{1}{[\text{HSO}_3^-]_t} \right) \tag{5}$$

RESULTS AND DISCUSSION

The experimental second- and third-order rate coefficients were calculated and the results are listed in Table 1. In most cases the second-order rate coefficients decreased and the third-order rate coefficients increased slightly (more clearly in the former case) towards the end of the runs, which suggests that the real order of the reaction is between two and three. The same idea is supported by the fact that when the initial concentration of hydrogen sulfite was altered systematically in the case of 2-methyl-*endo*-2-norbornenol (IV, Table 1),  $k_2$  again increased and  $k_3$  decreased with increasing HSO<sub>3</sub><sup>-</sup> concentration, the trend being more distinct in the former case:  $k_2 = (2.0 \pm 0.3) [\text{HSO}_3^-]_0 + (0.006 \pm 0.004)$  and  $k_3 = -(60 \pm 20) [\text{HSO}_3^-]_0 + (3.85 \pm 0.25)$ . The same kind of variation of the second-order rate coefficient with varying HSO<sub>3</sub><sup>-</sup> concentrations has also

Table 1. Apparent second- and third-order rate coefficients for disappearance of 2-norbornenols and 2-norbornenylmethanols in aqueous sodium hydrogen sulfite solutions (pH=5.0).

Substrate	Temp. °C	[ROH] <sub>0</sub> 10 <sup>-3</sup> M	[HSO <sub>3</sub> <sup>-</sup> ] <sub>0</sub> 10 <sup>-3</sup> M	k <sub>2</sub> 10 <sup>-4</sup> M <sup>-1</sup> s <sup>-1</sup>	k <sub>3</sub> M <sup>-2</sup> s <sup>-1</sup>
I	15	6.51	10.42	3.50 ± 0.07	4.24 ± 0.12
	15	6.74	10.79	3.21 0.07	4.02 0.09
	25	6.58	10.55	6.20 0.13	7.90 0.11
	25	6.81	10.86	7.35 0.14	9.06 0.27
	35	6.76	10.00	6.02 0.22	7.64 0.13
	35	6.66	10.48	6.58 0.07	8.00 0.27
	35	6.70	10.69	5.85 0.07	7.23 0.22
	35	6.70	10.69	5.85 0.07	7.23 0.22
II	15	8.33	13.32	0.85 ± 0.03	0.77 ± 0.03
	25	8.62	13.81	1.92 0.04	1.81 0.07
	35	8.53	13.63	4.71 0.05	4.00 0.10
III	15	7.71	12.35	2.23 ± 0.08	2.85 ± 0.21
	25	7.81	12.48	3.47 0.05	3.94 0.17
	35	7.71	12.35	5.93 0.09	6.21 0.14
	35	7.71	12.35	6.00 0.18	6.56 0.20
IV	5	8.50	13.58	0.66 ± 0.02	0.59 ± 0.02
	15	8.01	12.84	1.26 0.06	1.28 0.04
	25	4.99	5.00	1.57 0.06	3.53 0.18
	25	5.27	5.27	1.56 0.09	3.59 0.18
	25	5.62	10.00	3.03 0.10 <sup>a</sup>	3.68 0.10 <sup>a</sup>
	25	7.27	11.63	2.17 0.07 <sup>b</sup>	2.74 0.11 <sup>b</sup>
	25	7.55	12.09	2.85 0.14	2.90 0.14
	25	4.93	15.00	3.93 0.15	3.04 0.09
	25	7.13	22.83	5.01 0.21	2.54 0.08
	35	6.06	9.69	4.57 0.15	5.69 0.21
V	5.3	3.02	9.93	4.13 ± 0.08 <sup>b</sup>	4.82 ± 0.10 <sup>b</sup>
	15	3.24	10.00	7.33 0.11 <sup>b</sup>	8.56 0.23 <sup>b</sup>
VI	25	3.18	9.93	14.8 0.2 <sup>b</sup>	17.9 0.4 <sup>b</sup>
	15	3.78	9.55	2.22 ± 0.05 <sup>b</sup>	2.59 ± 0.11 <sup>b</sup>
	25	4.73	9.34	4.09 0.15 <sup>b</sup>	5.00 0.21 <sup>b</sup>
VII	35	3.83	10.00	7.48 0.17 <sup>b</sup>	8.60 0.22 <sup>b</sup>
	15	4.70	10.00	2.78 ± 0.02 <sup>b</sup>	3.27 ± 0.12 <sup>b</sup>
	25	4.56	10.00	5.93 0.16 <sup>b</sup>	6.58 0.12 <sup>b</sup>
VIII	35	4.03	10.00	12.7 0.2 <sup>b</sup>	15.6 0.5 <sup>b</sup>
	15	3.83	10.00	3.67 ± 0.18 <sup>b</sup>	3.81 ± 0.33 <sup>b</sup>
	25	3.82	6.11	6.22 0.27 <sup>a,b</sup>	11.6 0.4 <sup>a,b</sup>
35	3.80	6.08	9.89 0.20 <sup>b</sup>	20.1 0.6 <sup>b</sup>	

<sup>a</sup> Addition of hydroquinone (0.01 M) stopped the reaction. <sup>b</sup> The volume of 1 cm<sup>3</sup> of dioxane was added into 39 cm<sup>3</sup> of the reaction medium.

been observed in the reaction of hydrogen sulfite (or sulfite) ion with methacrylonitrile and methyl methacrylate.<sup>5</sup>

The rate coefficients increased generally with elevating temperature giving fairly linear log *k* vs. 1/*T* plots in most cases. A clear exception to this was observed in the reaction of *exo*-2-norbornenol (I, Table 1), where the rate coefficients (both *k*<sub>2</sub> and *k*<sub>3</sub>) were smaller at 35 °C than at 25 °C. The observation requires further investigation. In the reaction of 2-methyl-*endo*-2-norbornenylmethanol (VIII, Table 1) the log *k*<sub>2</sub> vs. 1/*T* plot was also curved,

but in this case the reason may be that the initial HSO<sub>3</sub><sup>-</sup> concentration at 15 °C differs from those at 25 and 35 °C. A curved Arrhenius plot has also been reported for acrylonitrile.<sup>5</sup>

The apparent activation parameters are given in Table 2 together with the rate coefficients at 25 °C computed from them. They are of the same order of magnitude as those calculated for the second-order ionic addition of SO<sub>3</sub><sup>2-</sup> ion to acrylonitriles and methyl acrylates.<sup>5</sup> The rates are thus surprisingly high for simple olefins (half-lives are from 14 to 140 min when calculated from the *k*<sub>2</sub>

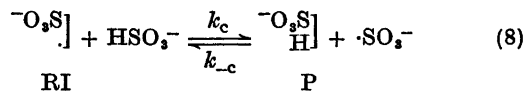
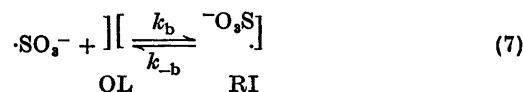
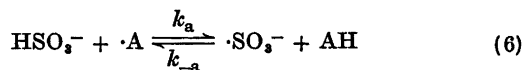
Table 2. Apparent activation parameters for the addition of sodium hydrogen sulfite to the double bond of some 2-norbornenols and 2-norbornenylmethanols and apparent rate coefficients at 25 °C calculated from them.

Substrate	$\Delta H^\ddagger/\text{kJ mol}^{-1}$		$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$		$k_2$ $10^{-3} \text{ M}^{-1} \text{ s}^{-1}$	$k_3$ $\text{M}^{-2} \text{ s}^{-1}$
	from $k_2$	from $k_3$	from $k_2$	from $k_3$		
I <sup>a</sup>	47.5 ± 6.8	48.8 ± 5.2	-108 ± 23	-64 ± 18	6.57 ± 0.46	8.46 ± 0.44
II	60.8 ± 2.9	58.2 ± 0.0	-74 ± 10	-45 ± 0	2.01 ± 0.07	1.81 ± 0.01
III	33.8 ± 2.8	27.2 ± 3.9	-159 ± 10	-142 ± 13	3.63 ± 0.11	4.19 ± 0.18
IV	44.2 ± 1.6	52.4 ± 2.4	-127 ± 5	-60 ± 8	2.53 ± 0.07	2.89 ± 0.12
V	42.2 ± 3.1	42.7 ± 4.1	-120 ± 11	-78 ± 14	14.4 ± 0.8	17.3 ± 1.3
VI	42.3 ± 0.7	41.8 ± 1.6	-129 ± 2	-91 ± 5	4.14 ± 0.03	4.88 ± 0.09
VII	53.5 ± 1.1	55.1 ± 4.6	-89 ± 4	-44 ± 15	6.04 ± 0.08	7.07 ± 0.36
VIII	34.1 ± 0.7	39.5 <sup>b</sup>	-153 ± 2	-92 <sup>b</sup>	6.16 ± 0.04	11.6

<sup>a</sup> Calculated from the rate coefficients at 15 and 25 °C. <sup>b</sup> Calculated from the rate coefficients at 25 and 35 °C.

values at 25 °C in Table 2 by employing 0.01 M initial concentrations for the reactants). The effect of the substituent(s) at C-2 upon the addition rates of HSO<sub>3</sub><sup>-</sup> seems to be fairly small, as was also observed in the proton addition to the double bond of the same substrates in aqueous perchloric acid.<sup>12,14,15</sup>

A formal kinetics for the addition of hydrogen sulfite *via* an oxygen-initiated free-radical mechanism to olefins, such as 2-norbornenols and 2-norbornenylmethanols, was derived by assuming the following scheme (*cf.* Refs. 1–5, 9–11, and 19):



where  $\cdot\text{A}$  is an initiating agent, *e.g.* oxygen dissolved in the reaction medium, OL is an olefinic substrate, RI is a free-radical intermediate, and P is a product. By assuming all steps (6)–(8) reversible and by employing the steady-state approximation for the concentrations of  $\cdot\text{SO}_3^-$  and the intermediate RI, the following expression was obtained for the disappearance rate of the olefinic OL:

$$-\frac{d[\text{OL}]}{dt} = \frac{k_a[\cdot\text{A}][\text{HSO}_3^-](k_b k_c [\text{HSO}_3^-][\text{OL}] - k_{-b} k_{-c} [\text{P}])}{k_{-a} [\text{AH}](k_{-b} + k_c [\text{HSO}_3^-])} \quad (9)$$

Since the reaction proceeded to the end completely and addition of acid or base did not regenerate any of the substrate, it can be concluded that  $k_{-b} k_{-c} [\text{P}] \ll k_b k_c [\text{HSO}_3^-][\text{OL}]$ . Since the initiating agent  $\cdot\text{A}$  is probably important only at the beginning of the run (the concentration of oxygen in the air saturated water is  $2.5 \times 10^{-4} \text{ M}$  at 25 °C and thus 2–5 % of the initial concentration of HSO<sub>3</sub><sup>-</sup>)<sup>20</sup> and AH is probably an unstable intermediate, the following approximation can be made:  $k_a[\cdot\text{A}]/k_{-a}[\text{AH}] = K = \text{constant}$ . Thus eqn. (9) is simplified to

$$-\frac{d[\text{OL}]}{dt} = \frac{K k_b k_c [\text{OL}][\text{HSO}_3^-]^2}{k_{-b} + k_c [\text{HSO}_3^-]} \quad (10)$$

This rate equation agrees well with the experimental data, since the second-order rate coefficient

$$k_2 = \frac{K k_b k_c [\text{HSO}_3^-]}{k_{-b} + k_c [\text{HSO}_3^-]} \quad (11)$$

decreases with decreasing HSO<sub>3</sub><sup>-</sup> concentration and the third-order rate coefficient

$$k_3 = \frac{K k_b k_c}{k_{-b} + k_c [\text{HSO}_3^-]} \quad (12)$$

increases with decreasing HSO<sub>3</sub><sup>-</sup> concentration. Thus the  $k_2$  and  $k_3$  values listed in Tables

1 and 2 are some kind of "apparent average" rate coefficients and are dependent on the  $\text{HSO}_3^-$  concentration in a way which depends on the mutual values of  $k_{-b}$  and  $k_c$ .

A rough estimate can be made for the ratio of  $k_{-b}/k_c[\text{HSO}_3^-]$  by plotting  $1/k_1$  vs.  $1/[\text{HSO}_3^-]_0$  and by calculating the ratio *slope/intercept* ( $=k_{-b}/k_c$ ). In the case of 2-methyl-endo-2-norbornenol (IV; correlation coefficient = 0.95) this kind of estimation gives the value of  $0.03 \pm 0.01$  for the ratio, which suggests that  $k_{-b}$  and  $k_c[\text{HSO}_3^-]$  are of the same order of magnitude, if  $[\text{HSO}_3^-] \approx 0.01$  M. Thus the order of reaction is really between two and three, which is in agreement with other kinetic data. Additional work on the subject is being carried out.

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