

comparison to identify the oil, VII, VIII, and IX, by means of paper chromatography. The yellow oil which remained after removal of solvent from part of the solution was reconverted to flavylium perchlorate as above.

Paper Chromatography of the Oil, VII, VIII, and IX.—Spots of dilute benzene solutions of the oil, VII, VIII, and IX, the oil from flavylium perchlorate and aqueous sodium bicarbonate, and 2-hydroxychalcone were applied to a strip of Whatman No. 1 paper. The spots were dried and the paper equilibrated for 45 min. with the atmosphere over the developing solvent in an airtight tank. The chromatogram was then developed at 30° with the aqueous (lower) layer of a 40% butanol–50% water–10% glacial acetic acid solvent system. The chromatogram was dried at 65° and the spots were detected under ultraviolet light. The results are given in Table II.

TABLE II

Compound		— R_f factors—		
Unknown oil	(3 spots)	0.038	0.21 ^a	0.22
Product from aq. NaHCO ₃				
and flavylium perchlorate	(3 spots)	0.038	0.21 ^a	.22
2-Hydroxychalcone	(1 spot)22

^a These spots were only detected at such high concentrations that the other spots were smeared. This fact, more than the R_f factors, indicates that the oils are composed of three components.

Ethyl N-(2-Phenyl-4H-1-benzopyran-4-ylidene)-phenylalaninate Hydroperchlorate.—Five grams (0.0163 mole) of flavylium perchlorate was suspended in a solution of 3.15 g. (0.0163 mole) of ethyl phenylalaninate in 110 ml. of chloroform. The mixture, which became green, was shaken 8 hr. and an insoluble precipitate was then filtered from the green mother liquor; weight 3 g.

The solid was recrystallized twice from glacial acetic acid. Light green crystals were obtained and washed with ether. The yield was 2.4 g. (30%), m.p. 233–234° dec.

Anal. Calcd. for C₂₆H₂₄O₃NClO₄: C, 62.97; H, 4.84; N, 2.82; ClO₄, 20.08. Found: C, 63.13; H, 5.09; N, 2.75; ClO₄, 20.38.

The green mother liquor was poured into 300 ml. of ether and a small quantity of a dark green gummy solid was filtered from the solution. This yellow solution deposited 0.6 g. of ethyl phenylalaninate hydroperchlorate after standing 4 hr. The solution

was then evaporated to dryness at room temperature and atmospheric pressure to yield 2 g. of a yellow oil (55%).

The reaction of 1 mole of flavylium perchlorate with 2 moles of ethyl phenylalaninate gave the ketimine hydroperchlorate in 14% yield, while the presence of Drierite increased the yield to 31%. The green gum was not a product of the latter two reactions.

Ethyl N-(2-Phenyl-4H-1-benzopyran-4-ylidene)-alaninate Hydroperchlorate.—The products from flavylium perchlorate and ethyl alaninate were obtained and purified as described above for ethyl phenylalaninate. The yield of ketimine hydroperchlorate was 2.1 g. (31%), from 0.0163 mole of each reactant, and the m.p. was 216–217° dec.

Anal. Calcd. for C₂₀H₂₀NO₃ClO₄: C, 56.94; H, 4.74; N, 3.32; ClO₄, 23.63. Found: C, 56.65; H, 4.57; N, 3.21; ClO₄, 23.24.

The oil (VII, VIII, IX) weighed 1 g. (27%).

Ethyl N-(2-Phenyl-4H-1-benzopyran-4-ylidene)-phenylalaninate and Alaninate.—Two grams of the respective imine hydroperchlorates were each suspended in 50 ml. of 2 N sodium hydroxide to which 50 ml. of ether was added. The mixtures were shaken 15 min. The ether layers were separated, washed once with 50 ml. of water, and the solvents were then evaporated at room temperature and atmospheric pressure. The resulting oil from flavone ethyl alaninate imine and the yellow solid from the flavone ethyl phenylalaninate imine were each recrystallized from petroleum ether (b.p. 60–100°) to yield white crystals. The yield of flavone ethyl alaninate imine was 0.67 g. (45%), m.p. 74.5–76°.

Anal. Calcd. for C₂₀H₁₉NO₂: C, 74.76; H, 5.92; N, 4.35. Found: C, 74.48; H, 5.52; N, 4.41.

The yield of flavone ethyl phenylalaninate imine was 0.96 g. (60%), m.p. 119.5–120.5°.

Anal. Calcd. for C₂₆H₂₃O₃N: C, 78.84; H, 5.79; N, 3.52. Found: C, 78.69; H, 5.69; N, 3.43.

The flavone ethyl alaninate imine was apparently somewhat unstable because discoloration appeared after the compound was exposed to the atmosphere for 5 to 8 hr.

Hydrogen Sulfide and the Flavone Ketimines.—The ethyl N-(2-phenyl-4H-1-benzopyran-4-ylidene)-phenylalaninate and alaninate gave 4-thioflavone in 76 and 48% yields, respectively. The procedure is given above. The 4-thioflavone melting points and mixture melting points checked.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, EASTMAN KODAK CO., ROCHESTER, N. Y.]

The Kinetics of Displacement of Halides from Substituted Quinones by Sulfite

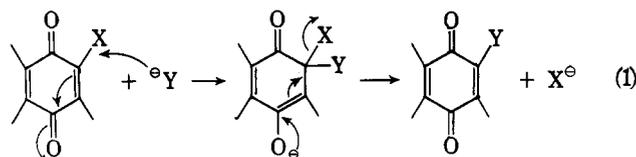
BY C. A. BISHOP, R. F. PORTER, AND L. K. J. TONG

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The displacement of halide from a series of 2-halo-3,5,6-trimethyl-*p*-benzoquinones by sulfite was preceded in two cases by a faster reversible quinone–bisulfite reaction. The rates of both reactions were dependent on the concentrations of sulfite rather than bisulfite and were general-acid catalyzed. Related mechanisms for the two reactions are proposed. The order of displacement rates is I⁻ >> Br⁻ > Cl⁻. A description of the apparatus used in the study of some fast reactions is included.

Quinones are known to undergo several types of reactions, including 1,4-additions,^{1–10} nucleophilic displacement of labile substituents,^{8–17} and oxidation–reduction reactions.^{2,3,5} No thorough kinetic study of these reactions has been reported, although a mechanism has

been proposed for nucleophilic displacement based on observed products (eq. 1).^{13,16,17}



Since the reaction involved replacement of the labile substituent (X) by a nucleophile (Y), the latter was assumed to add to the quinone at the substituted position, generating an intermediate stabilized by negative charge on the oxygen in the 4-position, as shown. Elimination of X in the second step completed the scheme.

To investigate the various steps of nucleophilic displacement of halides on quinones by sulfite, a series of 2-substituted-3,5,6-trimethyl-*p*-benzoquinones, including 2,3,5-trimethyl-*p*-benzoquinone and duroquinone, were treated with sulfite and the kinetics were measured. Alkyl substituents on the 3-, 5-, and 6-positions simpli-

- (1) J. W. Dodgson, *J. Chem. Soc.*, 2435 (1914).
- (2) J. M. Snell and A. Weissberger, *J. Am. Chem. Soc.*, **61**, 450 (1939).
- (3) T. H. James and A. Weissberger, *ibid.*, **61**, 442 (1939).
- (4) R. H. Thomson, *J. Org. Chem.*, **16**, 1082 (1951).
- (5) J. E. LuValle, *J. Am. Chem. Soc.*, **74**, 2970 (1952).
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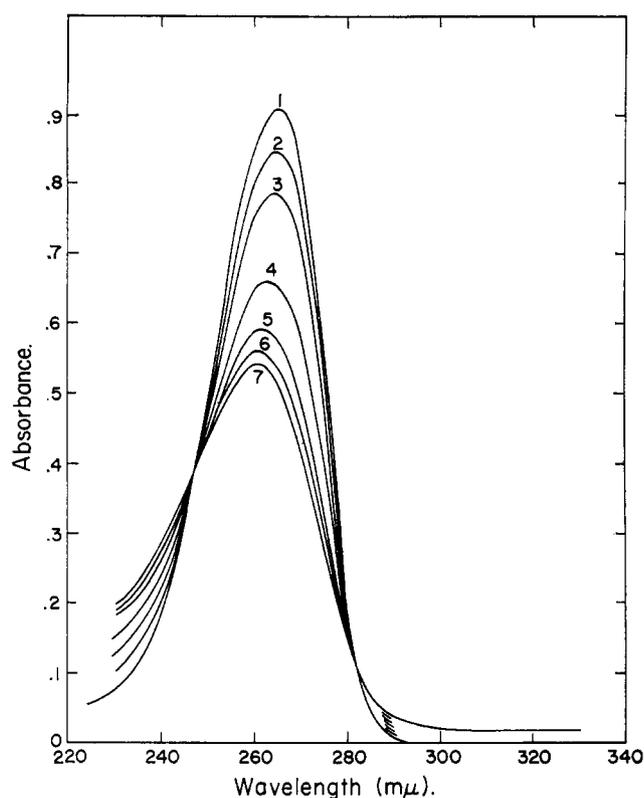
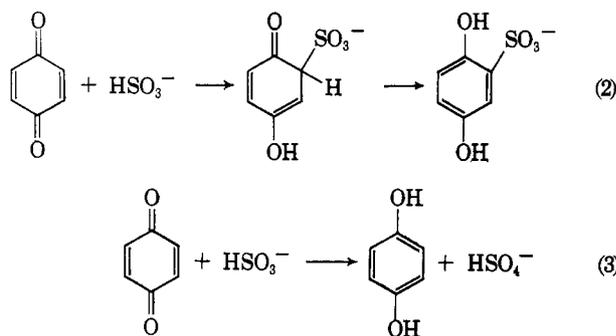


Fig. 1.—Change in the absorption of duroquinone ($5 \times 10^{-5} M$) in the presence of bisulfite at pH 7: (HSO_3^-) = 0.00 (1); 1.8×10^{-5} (2); 3.2×10^{-5} (3); 1.6×10^{-4} (5); 1.5×10^{-3} (6); 0.01 (7).

fied the kinetics by preventing reduction *via* 1,4-addition (eq. 2).

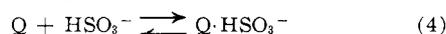


Fortunately, interference by the oxidation-reduction reaction in eq. 3 was also eliminated. We have found that nucleophilic displacement of bromide and chloride is preceded by a faster reversible sulfite-quinone reaction, which is also exhibited by duroquinone and trimethylquinone.

The quinone-sulfite equilibria will be described first since the results of this study are used in the analysis of the displacement reaction.

Data and Results

A. Quinone-Bisulfite Adduct Formation.—The initial rapid reaction between sulfite and most quinones is reversible and the rate is dependent on the nature of the acids present. The equilibrium can be represented as formally involving bisulfite ion and an adduct



where Q and $Q \cdot \text{HSO}_3^-$ represent the quinone and quinone-bisulfite adduct, respectively. For example, Fig. 1 shows the ultraviolet absorption curves at equilibrium

of mixtures of duroquinone and bisulfite at constant pH, the concentration of the bisulfite varying from zero (curve 1) to 0.01 M (curve 7). The absorption near 260 $m\mu$ decreased with increasing bisulfite and approached a lower limit. In every case, this final absorption had $\lambda_{D_{\max}}$ at slightly shorter wave length and a molar extinction coefficient roughly one-half that of the original quinone (Table I). Curve 1 (Fig. 1) represents pure Q and curve 7 represents $> 99\%$ $Q \cdot \text{HSO}_3^-$. A given set of absorption measurements as in Fig. 1 produced a single equilibrium constant, $K = [Q][\text{HSO}_3^-]/[Q \cdot \text{HSO}_3^-]$. These constants are reported in Table I for $\mu = 0.225$ and were the same at $\mu = 0.065$ for the bromoquinone and chloroquinone.

TABLE I
ULTRAVIOLET ABSORPTION MAXIMA AND EQUILIBRIUM
CONSTANTS FOR VARIOUS 2-SUBSTITUTED-3,5,6-TRIMETHYL-
p-BENZOQUINONES

R	Quinone		Quinone-bisulfite adduct		K^a
	$\lambda_{D_{\max}}$	ϵ , l./mole cm.	$\lambda_{D_{\max}}$	ϵ , l./mole cm.	
CH ₃	265	18300	261	11000	8.6×10^{-6}
	270	18300			
H	260	20000	260	10800	$< 3 \times 10^{-6}$
Cl	274	18700	265	11300	1.45×10^{-4}
Br	279	15700	266	9800	5.8×10^{-6}
	249	7390			
-SO ₃ Na	260	15200	263	11000	1.28×10^{-4}

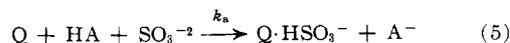
$$^a K = [Q][\text{HSO}_3^-]/[Q \cdot \text{HSO}_3^-].$$

The reversibility of the reaction was demonstrated by the recovery of the quinone absorption when the bisulfite concentration was lowered either by the addition of formaldehyde or by raising the pH.

Evidence that the intermediate is an adduct and not the corresponding reduction product (eq. 3) is the observations of the reversibility of the reaction and the differences between the spectra of the intermediate and the corresponding hydroquinone. For example, duroquinone has a maximum absorption at 276 $m\mu$ with $\epsilon \sim 2 \times 10^3$.

For equilibrium measurements, the bisulfite concentration was kept low in order to obtain measurable concentrations of both Q and $Q \cdot \text{HSO}_3^-$. For the rate measurements, the bisulfite concentration was raised to higher levels to force the reaction to near completion. The reverse reactions can then be ignored in the calculations.

The forward rates under varying conditions of pH and buffer and sulfite concentrations are reported as pseudo-first-order constants, k_a , for the disappearance of quinone, in Tables II-V. The data reveal not only a first-order dependence on sulfite, but also a linear decrease in rate when phosphate buffer is replaced by potassium chloride at constant pH. The kinetics agree with the scheme shown



where HA is the conjugate acid of the base A^- . The acid catalytic constants for each acid, $k_{\text{HA},a} = k_a/(\text{SO}_3^{2-})(\text{HA})$, are given in Table VI.

TABLE II
KINETIC DATA FOR THE REACTION OF DUROQUINONE WITH SULFITE

pH	$\frac{H_2PO_4^-}{HPO_4^{2-}}$	$H_2PO_4^- + HPO_4^{2-}, M$	$HSO_3^- + SO_3^{2-}$		$k_a, \text{sec.}^{-1} \times 10^3$
			$M \times 10^3$	$M \times 10^3$	
5.41	20.5	0.2041	9.82	0.420	0.882
		.1531	9.80	.422	.698
		.1021	9.75	.417	.511
		.0510	9.80	.422	.346
6.18	3.55	.1566	9.80	2.04	2.48
		.1174	9.65	2.01	2.04
		.0783	9.65	2.01	1.49
		.0391	9.76	2.03	0.963
6.72	1.00	.1094	9.80	4.67	3.12
		.0820	9.80	4.67	2.47
		.0547	9.80	4.67	1.95
		.0273	9.80	4.67	1.27
7.02	0.507	.0969	9.76	6.16	2.94
		.0727	9.73	6.15	2.41
		.0485	9.68	6.12	1.87
		.0242	9.65	6.09	1.29
7.02	.507	.0969	7.20	4.56	2.15
		.0727	7.20	4.54	1.72
		.0485	7.20	4.60	1.33
			7.18	4.54	0.40
7.01	.507	.0485	6.01	3.80	1.08
		.0969	4.83	3.05	1.45
		.0727	4.80	3.04	1.12
		.0485	4.80	3.02	0.82
7.01	.507	.0485	2.38	1.50	.40
			2.32	1.47	.075
			9.70	9.38	.768
			9.70	9.38	.664
8.23	.0309	.0767	9.70	9.38	.664
		.0575	9.70	9.38	.579
		.0384	9.70	9.38	.484
		.0191	9.70	9.38	.484

TABLE III

KINETIC DATA FOR THE REVERSIBLE BISULFITE ADDITION REACTION OF 2-BROMO-3,5,6-TRIMETHYL-*p*-BENZOQUINONE

pH	$\frac{H_2PO_4^-}{HPO_4^{2-}}$	$H_2PO_4^- + HPO_4^{2-}, M$	$HSO_3^- + SO_3^{2-}$		$k_a, \text{sec.}^{-1}$
			$M \times 10^3$	$M \times 10^3$	
4.51	20.9	0.2041	9.55	0.407	0.55
		.1531	9.55	.407	.48
		.1021	9.55	.407	.44
5.81	8.12	.200	9.50	.959	1.00
		.150	9.50	.959	0.900
		.100	9.50	.959	0.819
6.10	4.17	.157	9.42	1.71	1.83
		.118	9.49	1.72	1.59
		.078	9.49	1.72	1.30
6.91	0.662	.0960	9.24	5.36	3.35
		.0720	9.23	5.36	2.99
		.0480	9.29	5.38	2.23
		.0240	9.20	5.34	1.95
			9.32	5.40	1.18

B. Displacement Reactions.—The ultraviolet spectra of the products of sulfite displacement indicated that all three halotrimethyl-*p*-benzoquinones gave the same quinonoid product, which further formed a bisulfite adduct in the presence of excess sulfite (Table I). The product could not be isolated, but infrared analysis of some crude material indicated the presence of $-SO_3Na$. The quinonoid product is assumed to be 2-sulfo-3,5,6-trimethyl-*p*-benzoquinone (I).

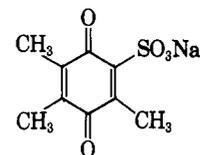


TABLE IV

KINETIC DATA FOR THE REVERSIBLE BISULFITE ADDITION REACTION OF 2-CHLORO-3,5,6-TRIMETHYL-*p*-BENZOQUINONE

pH	$\frac{H_2PO_4^-}{HPO_4^{2-}}$	$H_2PO_4^- + HPO_4^{2-}, M$	$HSO_3^- + SO_3^{2-}$		$k_a, \text{sec.}^{-1}$
			$M \times 10^3$	$M \times 10^3$	
5.87	7.0	0.178	2.45	0.286	0.123
			2.45	.286	.105
			2.45	.286	.088
			2.45	.286	.059
6.21	3.58	.1538	2.45	.546	.205
			2.45	.546	.160
			2.45	.546	.131
			2.45	.546	.091
6.80	0.835	.1011	2.45	1.28	.328
			2.45	1.28	.275
			2.45	1.28	.210
			2.45	1.28	.138
7.21	0.489	.0935	2.45	1.69	.310
			2.45	1.69	.250
			2.45	1.69	.216
			2.45	1.69	.146

TABLE V

KINETIC DATA FOR THE REVERSIBLE BISULFITE ADDITION REACTION OF 2-SULFO-3,5,6-TRIMETHYL-*p*-BENZOQUINONE

pH	$\frac{H_2PO_4^-}{HPO_4^{2-}}$	$H_2PO_4^- + HPO_4^{2-}, M$	$HSO_3^- + SO_3^{2-}$		$k_a, \text{sec.}^{-1}$
			$M \times 10^3$	$M \times 10^3$	
5.46	18.7	0.2041	4.90	0.245	0.0292
			4.90	0.245	.0249
			4.90	1.11	.135
6.21	3.59	.1566	4.90	1.11	.125
		.1174	4.90	1.11	.115
		.0783	4.90	1.11	.115
7.09	0.437	.0969	2.45	1.68	.180
		.0485	2.45	1.68	.155

TABLE VI

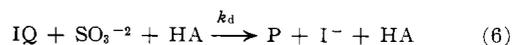
ACID CATALYTIC CONSTANTS k_{HA} FOR QUINONE-SULFITE REACTIONS

Quinone	$k_{H_2PO_4^-}$	$k_{HPO_4^{2-}}$	$k_{HSO_3^-}$	$k_{H_3O^+}$	$k_{H_2O^a}$
Duroquinone	9.2	0.02	15.8	6.6×10^4	0.0008
2-Bromo-3,5,6-trimethyl- <i>p</i> -benzoquinone	2000	7700	30000	2×10^8	1
2-Chloro-3,5,6-trimethyl- <i>p</i> -benzoquinone	1570	1700	10700	7.3×10^7	0.7
2-Sulfo-3,5,6-trimethyl- <i>p</i> -benzoquinone	200	460	2000	10^8	1.4

^a $[H_2O]$ assumed to be 55 *M*.

2-Iodo-3,5,6-trimethyl-*p*-benzoquinone (IQ).—The rate of release of iodide as measured by titration with silver nitrate was equal to the rate of disappearance of the iodoquinone as measured by the decrease in absorption at 286 $m\mu$, showing that no bisulfite adduct was observed in this case. Either the rate of halide displacement is much faster than adduct formation or the quinone-bisulfite adduct equilibrium lies far to the side of free quinone.

Examination of Table VII shows the pseudo-first-order rates, k_a , are dependent on the phosphate buffer as well as on the sulfite concentrations



where IQ, P, and HA are the iodoquinone, sulfoquinone, and a particular acid, respectively. The individual constants for each of the acids are reported in Table XI.

TABLE VII
KINETIC DATA FOR THE DISPLACEMENT OF IODIDE FROM
2-iodo-3,5,6-trimethyl-*p*-benzoquinone BY SULFITE IN
AQUEOUS SOLUTION

pH	H ₂ PO ₄ ⁻ HPO ₄ ⁻²	Total phosphate concn., <i>M</i>	HSO ₃ ⁻ +		Rate, sec. ⁻¹
			SO ₃ ⁻² , <i>M</i> × 10 ³	[SO ₃ ⁻²], <i>M</i> × 10 ³	
5.61	19.0	0.0590	4.9	0.219	0.197
		.0442	4.9	.219	.164
		.0295	4.9	.219	.134
		.0148	4.9	.219	.112
6.38	3.16	.0452	4.9	1.0	.616 ^a
6.38	3.16	.0452	4.9	1.0	.605
7.23	0.457	.0339	4.9	1.0	.485
		.0226	4.9	1.0	.422
		.0277	2.45	1.58	.460
		.0208	2.45	1.58	.380
		.0139	2.45	1.58	.350
		.0069	2.45	1.58	.283
	0.457	.0264	4.9	3.16	.930

^a This value was determined by quenching the reaction with acid and titrating it with silver nitrate. All other values were determined spectrophotometrically.

TABLE VIII
SLOPE AND INTERCEPT OF $k_d/(\text{SO}_3^{-2})$ vs. PHOSPHATE BUFFER
CONCENTRATION FOR REACTION OF 2-iodo-3,5,6-trimethyl-*p*-
benzoquinone

pH	Slope (l. ² /mole ² sec.)	Intercept (l./mole sec.)
5.61	8780	357
6.38	7800	240
7.23	5085	142

TABLE IX
KINETIC DATA FOR THE DISPLACEMENT OF BROMIDE FROM 2-bromo-3,5,6-trimethyl-*p*-benzoquinone BY SULFITE IN AQUEOUS
SOLUTION

pH	Sulfite buffer added, <i>M</i> × 10 ³	Equil. concn., <i>M</i> × 10 ^{3a}			$\frac{\text{BrQ}}{\text{BrQ}}$	$k_d' \times 10^3$, sec. ⁻¹	<i>R</i>	<i>R</i> (reconstructed)
		BrQ·HSO ₃ ⁻	(HSO ₃ ⁻)	(SO ₃ ⁻²)				
6.00	49.0	0.4	43.8	4.77	763	0.471	75.2	77.2
6.55	37.3	.4	26.6	10.3	464	.941	42.3	39.2
7.00	28.5	.4	13.6	14.5	239	1.16	19.2	20.9
7.50	23.5	.4	5.5	17.6	90.3	2.13	10.9	10.8
8.15	22.0	.4	1.23	20.4	22.2	5.37	5.8	5.8
8.15 ^b	8.23	.36	0.45	7.42	8.7	4.00	4.7	5.0

^a Concentrations of sulfite species at the start of the displacement reaction. ^b The ionic strength was adjusted with KNO₃ in this sample.

TABLE X
KINETIC DATA FOR THE DISPLACEMENT OF CHLORIDE FROM 2-chloro-3,5,6-trimethyl-*p*-benzoquinone BY SULFITE IN AQUEOUS
SOLUTION

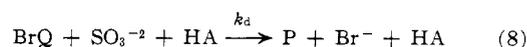
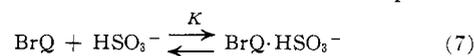
pH	Sulfite buffer added, <i>M</i> × 10 ³	Equil. concn., <i>M</i> × 10 ^{3a}			$\frac{\text{ClQ}}{\text{ClQ}}$	$k_d' \times 10^3$, sec. ⁻¹	<i>R</i>	<i>R</i> (reconstructed)
		ClQ·HSO ₃ ⁻	(HSO ₃ ⁻)	(SO ₃ ⁻²)				
6.00	49.0	0.4	43.8	4.77	304	0.1575	10.0	10.0
6.52	37.3	.4	26.7	10.2	178	.446	7.68	7.6
6.95	28.5	.4	14.1	14.1	98	.995	6.94	6.96
7.50	23.5	.4	5.5	17.6	38.9	3.03	6.70	6.42
8.15	22.0	.4	1.23	20.4	9.48	13.7	6.35	6.35
8.20 ^b	8.23	.32	0.43	7.48	3.96	12.1	6.41	6.32

^a Concentrations of sulfite species at the start of the displacement reaction. ^b The ionic strength was adjusted with KNO₃ in this sample.

2-Bromo-3,5,6-trimethyl-*p*-benzoquinone (BrQ) and 2-Chloro-3,5,6-trimethyl-*p*-benzoquinone (ClQ).—The displacement of halide from the bromoquinone and chloroquinone was preceded by a faster, reversible formation of quinone-bisulfite adduct. This quinone-bisulfite adduct equilibrium was established before 2% of the halide was displaced. The rates were measured by following the increase in halide concentration with a silver-silver halide electrode. The methods used for the iodoquinone were not applicable because dilute bromide and chloride concentrations could not be titrated

with sufficient accuracy for the rate calculations and the absorptions of the bromoquinone and chloroquinone species were too close to those of the products.

The pseudo-first-order rates, k_d' , reported in Tables IX and X, were measured in aqueous solutions where the sulfite-bisulfite acted as the pH buffer. The data for both quinones were analyzed according to the same scheme, which is illustrated here for the bromoquinone.



BrQ and BrQ·HSO₃⁻ represent the concentrations of bromoquinone and bromoquinone-bisulfite adduct, respectively. The fourth and fifth columns in Tables IX and X give the effective bisulfite and sulfite concentrations, respectively, for the displacement reaction. The part of the sulfite buffer existing as quinone-bisulfite adducts was calculated from the equilibrium constants, *K*.

The rapid quinone-bisulfite equilibrium (eq. 7) also decreased the effective quinone concentration in the reaction so that k_d' had to be corrected for the quinone which existed as BrQ·HSO₃⁻. Analysis of the data led to a sum, *R*, of the individual constants due to each acid times the acid concentrations. The individual rate constants were calculated from *R* and are reported in Table XI.

Calculations

A. Quinone-Bisulfite Adduct Formation.—The pseudo-first-order rates of quinone-bisulfite adduct

formation were calculated from absorption measurements as follows and resolved into individual acid constants. From eq. 5, we obtain

$$d(Q)/dt = -k_a(Q) \quad (9)$$

so

$$d \ln(Q)/dt = -k_a \quad (10)$$

where

$$k_a = (\text{SO}_3^{-2}) \sum_i k_{\text{HA}_i, \text{a}}(\text{HA}_i) \quad (11)$$

a constant when (SO₃⁻²) and (HA) are in large excess.

TABLE XI
ACID CATALYTIC CONSTANTS, k_{HA_i} , IN THE SULFITE
DISPLACEMENT OF HALIDE FROM 2-HALO-3,5,6-TRIMETHYL-*p*-
BENZOQUINONES

Acid	Iodoquinone ($l.^2/mole^2 \text{ sec.}$)	Bromoquinone ($l.^2/mole^2 \text{ sec.}$)	Chloroquinone ($l.^2/mole^2 \text{ sec.}$)
H ₃ O ⁺	4.9×10^7	2.9×10^7	2.5×10^6
H ₂ O	2.1 ^a	0.08 ^a	0.115 ^a
HSO ₃ ⁻	2.65×10^4	1×10^3	27
H ₂ PO ₄ ⁻	9.15×10^3		
HPO ₄ ⁻²	3.23×10^3		

^a The molarity of water was assumed to be 55.

Even though the spectral absorption was due to both Q and Q·HSO₃⁻, it can be shown that the equation

$$-2.303 \frac{d \log (D - D_c)}{dt} = k_a \quad (12)$$

holds, where D is the absorption of the mixture after some time, t , and D_c is the limiting density, as defined in the Experimental section. All rates were measured at the $\lambda_{D_{max}}$ of the quinone.

The pseudo-first-order rate constants, k_a , after being divided by (SO_3^{2-}) were plotted against the total phosphate concentration. At constant pH and ionic strength, the resulting slope is a measure of the contribution of phosphate terms to the over-all rate and the intercept includes all the other acid terms.

$$\text{slope} = \frac{k_{H_2PO_4^-}(H_2PO_4^-) + k_{HPO_4^{2-}}(HPO_4^{2-})}{(H_2PO_4^-) + (HPO_4^{2-})} \quad (13)$$

$$\text{intercept} = k_{HSO_3^-}(HSO_3^-) + k_{H_3O^+}(H_3O^+) + k_{H_2O}(H_2O) \quad (14)$$

As an example, values of the slopes and intercepts of such plots for duroquinone at several different pH values are given in Table XII. Each set of values represents a different contribution from each of the terms, since the concentration of each of the acids (except water) changes with pH. The individual rate constants were calculated from simultaneous equations obtained from the data at the various pH's and using the appropriate pK 's for the acids.

TABLE XII

SLOPES AND INTERCEPTS OF PLOTS OF $k_a/[SO_3^{2-}]$ vs. $[H_2PO_4^-]$ + $[HPO_4^{2-}]$ FOR DUROQUINONE-SULFITE REACTION					
pH	5.41	6.18	6.72	7.02	8.23
Slope	8.22	6.44	4.79	3.88	0.51
Intercept	0.405	0.215	0.139	0.105	0.0435

B. Displacement Reactions.—For the displacement reaction of the iodoquinone illustrated in eq. 6, the rate can be expressed as

$$-d(IQ)/dt = (IQ)(SO_3^{2-}) \sum_i k_{HA_i}(HA_i) \quad (15)$$

With buffered solutions and excess sulfite, the rate was first order with respect to IQ

$$d \ln (IQ)/dt = -k_d \quad (16)$$

$$\text{with } k_d = (SO_3^{2-}) \sum_i k_{HA_i}(HA_i)$$

In eq. 16, (IQ) can be replaced by differences in optical density or differences in milliliters of titrant.

The data were analyzed in the same way as the quinone-bisulfite addition reactions. Slopes and intercepts of the $k_d/(SO_3^{2-})$ vs. total phosphate concentration plots are given in Table VIII and the individual rate constants due to each acid in Table XI.

Since the displacements of bromide and chloride from the corresponding quinones were preceded by a rapid quinone-bisulfite adduct equilibrium, a somewhat different approach was used in the analysis of the data. In the scheme represented by eq. 7 and 8, it is assumed

that sulfite does not react with the adduct to release halide, so the situation is similar to that of the IQ reaction and the total rate of release of bromide ion is (from eq. 8)

$$-d(\overline{BrQ})/dt = (BrQ)(SO_3^{2-}) \sum_i k_{HA_i}(HA_i) = d(Br^-)/dt \quad (17)$$

(\overline{BrQ}) is the total bromoquinone concentration, as defined by eq. 18.

$$(\overline{BrQ}) = (BrQ) + (BrQ \cdot HSO_3^-) = (Br^-)_\infty - (Br^-) \quad (18)$$

$(Br^-)_\infty$ and (Br^-) are, respectively, the concentrations of bromide at the end of the reaction and at any time during the reaction. To cast eq. 17 in more convenient form, it is divided by eq. 18

$$\frac{d(Br^-)}{[(Br^-)_\infty - (Br^-)]} dt = \frac{(BrQ)}{(BrQ)} (SO_3^{2-}) \sum_i k_{HA_i}(HA_i) = k_d' \quad (19)$$

where k_d' is the observed first-order rate constant for the liberation of Br⁻. The terms $(BrQ)/(BrQ)$, (SO_3^{2-}) , and (HA_i) can be obtained from known equilibrium constants. The terms $k_{HA_i}(HA_i)$ were evaluated by analysis of eq. 20.

$$\sum_i k_{HA_i}(HA_i) = k_d'(\overline{BrQ})/(BrQ)(SO_3^{2-}) = R \quad (20)$$

The ratio R was calculated for each run. These results are listed in Table IX. In the same way, the ratios were calculated for the chloroquinone, according to eq. 21.

$$\sum_i k_{HA_i}(HA_i) = k_d'(\overline{ClQ})/(ClQ)(SO_3^{2-}) = R \quad (21)$$

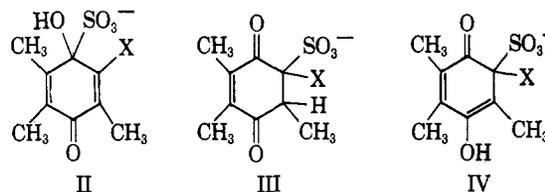
These results are included in Table X. Ratio R was the sum of only three products, since sulfite-bisulfite was the only buffer in the system.

$$R = k_{HSO_3^-} + k_{H_2O}(H_2O) + k_{H_3O^+}(H_3O^+) \quad (22)$$

The acid catalytic constants, k_{HA} , were obtained from the resulting simultaneous equations and are reported in Table XI. In each case, R was reconstructed from the calculated constants to show the fit of the data (Tables IX and X).

Discussion

A. Nature of the Quinone-Bisulfite Adducts.—The structure of the quinone-bisulfite adducts has not been established unambiguously, since these compounds could not be isolated. Conjectures have been made based on comparison of ultraviolet spectra and the bisulfite equilibria of the quinones and of some related compounds. Some suggested structures will serve as a basis for discussion.



The product of 1,4-addition (IV) can be eliminated immediately, since this chromophore is expected to absorb at much longer wave lengths than that observed. Woodward's rules predict a $\lambda_{D_{max}}$ of 338 $m\mu$. Reported conjugated dienones exhibit strong absorption in the range of 290–350 $m\mu$.¹⁸⁻²¹

Unfortunately, satisfactory predictions of $\lambda_{D_{max}}$ based on absorption rules cannot be made for structures II and

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sumed in the calculations to be unreactive toward displacement. This assumption may not be justified in view of the $\text{SN}2'$ reactivity of allylic systems,³² of which III is an example. Further work on these displacement reactions is necessary before a firm interpretation of $k_{\text{HSO}_3^-}$ can be made.

Nucleophilic attack at an unsubstituted position on a quinone usually results in a substituted hydroquinone. Some of these reactions are known to be catalyzed by strong acids.¹⁷ The first step is generally thought to be a 1,4-addition of the nucleophile and acid, followed by enolization, although the mechanism has not been established.³³ The results in this paper show that the first steps in quinone displacement reactions can also be interpreted as a 1,4-addition. However, in the displacement reaction, the presence of a substituent instead of a hydrogen atom at the position of nucleophilic attack precludes enolization, resulting instead in the elimination of the labile substituent and regeneration of the quinonoid structure. Furthermore, the mechanism proposed previously for displacement reactions (eq. 1) appears to be basically correct but, in addition, the electron withdrawal by the oxygen atom is probably aided by hydrogen bonding to an acid. Unless the observed displacement rates are corrected for bisulfite adduct formation, the iodide rate is much larger than the other two rates. For example, the observed relative rates, chloride:bromide:iodide, around pH 6 are 1:3:2000. However, if the rates are corrected for the assumed nonreactivity of the quinone-bisulfite adduct, the same relative rates near pH 6 are 1:7.5:60, and near pH 7 they are 1:3:30.

Preliminary results indicate that hydroxide ion is also a good nucleophile for these displacements, but it is only about 1/50 as reactive as sulfite.

Experimental

Preparation of Compounds. Duroquinone was a commercially available sample which was recrystallized from 95% ethanol; m.p. 110–111° (lit.³⁴ m.p. 110°).

Trimethyl-*p*-benzoquinone.—Ferric chloride oxidation of the purified hydroquinone and subsequent steam distillation gave a yellow solid. Distillation resulted in a yellow liquid, b.p. 115° (8 mm.), showing less than 0.2% of impurities by gas-phase chromatographic examination.

2-Chloro-3,5,6-trimethyl-*p*-benzoquinone.—Vigorous swirling of a suspension of trimethyl-*p*-benzoquinone (30 g.) in concentrated hydrochloric acid (100 ml.) gave a black precipitate. The yellow color was removed completely by maintaining the mixture at reflux for 3 hr. after dilution with water (100 ml.)—concentrated hydrochloric acid (50 ml.). The crude solid was dissolved in glacial acetic acid—water solution and aqueous sodium dichromate (100 g. in 100 ml.) was added in portions. After the mixture had stood for 15 min., a yellow solid was precipitated by dilution to 4 l. Crystallization from ethanol—water solution gave a yellow material, m.p. 64–65°; repeated recrystallization from petroleum ether gave yellow flakes, m.p. 76–77° (lit.³⁵ m.p. 72–73°).

2-Bromo-3,5,6-trimethyl-*p*-benzoquinone.—To a stirred solution of 2,4-dibromo-3,5,6-trimethylphenol³⁶ in glacial acetic acid (1500 ml.) at 70° there was added, in a slow stream, a solution of sodium dichromate (298 g.) in water (500 ml.). After the initial vigorous reaction and completion of addition, stirring was continued for 30 min. Dilution to 4 l. with water precipitated a yellow solid, which was crystallized from 90% ethanol; m.p. 78–80°. Recrystallization from ligroin gave yellow needles, m.p. 78–80° (lit.³⁷ m.p. 79–80°).

2-Iodo-3,5,6-trimethyl-*p*-benzoquinone was prepared by the action of iodine and hydrogen peroxide on 2,3,5-trimethylphenol, according to the method of Cressman.³⁸ Recrystallization several times from ligroin gave an orange solid, m.p. 71.5–73°.

2-Sulfo-3,5,6-trimethyl-*p*-benzoquinone.—Attempts to prepare the quinone by reaction of 2-iodo- or 2-bromo-3,5,6-trimethyl-*p*-benzoquinone with an equivalent amount of sodium sulfite resulted in a light yellow solid material whose infrared

spectrum indicated the presence of $-\text{SO}_3\text{Na}$. Attempts to isolate various salts were unsuccessful, as these substances showed considerable thermal instability.

Sulfonation or chlorosulfonation of trimethylhydroquinone led only to recovery of starting material.

Quinone-Bisulfite Adducts.—The quinones were soluble only to about 5×10^{-4} M in aqueous solution, and sodium bisulfite was soluble only in water, so a mixed-solvent method was employed, as in the following example: Trimethyl-*p*-benzoquinone (0.60 g., 0.004 mole) was dissolved in deaerated 95% ethanol (25 ml.) and added dropwise to a solution of $\text{Na}_2\text{S}_2\text{O}_3$ (0.39 g., 0.004 mole) and Na_2SO_3 (0.01 g.) in deaerated water (25 ml.). The yellow quinone color of the solution changed to light tan. The solution was left in a hood overnight and the solvent evaporated, leaving a yellow semisolid mass. More solvent was removed under vacuum in a desiccator where the mass finally became solid. Although it appeared dry at this point, infrared and nuclear magnetic resonance analyses indicated the presence of a large percentage of water and, indeed, the material was so hygroscopic that exposure to moist air produced a semisolid mass within 15 sec. Under these conditions, infrared and n.m.r. analyses were inconclusive and elemental analysis was of no value.

pK's of Acids.—For internal consistency, the pK's of monobasic phosphate ion and bisulfite ion used in the calculations of rate constants were determined from the pH's of the various known mixtures of the acid and conjugate base under the reaction conditions and using the same glass electrodes. In aqueous solution at $\mu = 0.225$, the pK of the HSO_3^- was 6.76 and that of the H_2PO_4^- was 6.70; at $\mu = 0.065$, $\text{p}K_{\text{HSO}_3^-} = 6.97$ and $\text{p}K_{\text{H}_2\text{PO}_4^-} = 6.87$. K_w was assumed to be $10^{-14.00}$.

Special Equipment.—Many of the reactions had half-times in the range of a few milliseconds to a few seconds. These rates were measured by a rapid mixing technique³⁹ using a modification of a machine which has already been described.⁴⁰ The new features include: (1) a double-beam type of spectrophotometer which can compensate for the absorption of the medium by placing the latter in the reference beam; (2) readings are obtainable directly in optical density units; (3) in the duration of a steady state of flow, the wave length of the light source can be varied and a continuous absorption curve produced on a recorder; (4) the range of measurement extends from the visible region to the ultraviolet; and (5) a switching mechanism is included which simultaneously stops the flow and starts the recorder so that absorption curves can be obtained over time intervals varying from a few seconds to 10 min.

Except for a few minor alterations in arrangement and in the control mechanism, the major improvements were the additions of a double-beam-type grating spectrophotometer and quartz windows on the cells, which extended the range of the machine into the ultraviolet region.

The spectrophotometer was assembled from commercially available units to which certain alterations were made. A Beckman dual source lamp unit with a Model 23700 DV power supply was used as a light source. A Farrand grating monochromator (Cat. No. 103420) was altered by installing a cylindrical chopper at the entrance slit, to give alternate upper and lower light beams through the monochromator to the exit slit. In operation, these two beams were directed through two absorption cells at the exit slit. The lower cell is a part of the flow channel from, and in close proximity to, the last mixing chamber. The upper cell is a part of the flow channel from a reservoir containing the solution blank. The light alternately passing through the two absorption cells falls upon a single photomultiplier tube. The amplifier for the photomultiplier tube is of the differential type, giving an output voltage proportional to the difference in the optical densities of the two solutions flowing through the absorption cells. A motor connected to the wave length drum of the monochromator can be used to sweep the entire spectral range in about 20 sec., during which time a constant flow rate is maintained through the mixing chambers and absorption cells. A multiturn potentiometer connected to the wave length drive generates an output voltage linear to the wave length of the light through the absorption cells. Using an X-Y recorder, the density vs. wave length plot of material flowing through the absorption cells can be recorded for the entire spectral range during one cycle of the mixing machine. As an alternative, the wave length may be maintained at a given setting and the density of the material in the absorption cell plotted as a function of time after stopping the flow through the cell.

In most of our experiments, the reactions were initiated by mixing more than two components; the premixing of components is impractical because of low stability. The machine was therefore provided with four separate sets of reservoir, piston, and valves, as well as three mixing chambers; and arranged so that a maximum of four solutions can be mixed consecutively with short

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time intervals between each mixing. For efficient mixing, a pair of solutions is pumped into each mixing chamber at equal flow rate. When only three solutions are used in the experiment, two reservoirs may be filled with the same solution to produce a high flow rate and, therefore, a short reaction time.

Three types of measurements can be made in this machine.

(1) **Steady-State Method.**—The reaction is started upon the addition of the last solution. A steady state of flow is maintained for 20 sec. so that an absorption curve of the flowing mixture in the cell is obtained. The reaction time is taken as the average time of flow from the last mixing chamber to the cell; this was calculated from the volume rate and the cross section of the channel. The method of calibration has been described previously.⁴⁰

(2) **Quenched-Flow Method.**—A reaction may be started in mixing chamber 2 upon the addition of solution 3 and quenched in mixing chamber 3 upon the addition of solution 4. The reaction time is taken as the average flow time between the two mixing chambers.

(3) **Stopped-Flow Method.**—For slower reactions with half-lives of a few seconds to a few minutes, a stopped-flow method may be used. After steady state of flow has been established, a switch is activated which simultaneously shuts off the valves (stops flow) and starts the travel of the recorder pen on the time axis. The optical density (at constant wave length) of the trapped solution is recorded *vs.* time.

General Reaction Conditions.—Solutions of sodium sulfite and sodium bisulfite decompose on standing in the presence of oxygen. All sulfite solutions were prepared using water which had been purged thoroughly with a stream of nitrogen, and subsequently were protected from air. All other solutions were deaerated before addition of sulfite and also were protected from air. The concentrations of sulfite stock solutions were determined iodometrically. All reaction runs were made at $25.0 \pm 0.1^\circ$. The pH of each reaction mixture was determined with a Beckman Model G pH meter and with the same glass electrode as that used in the *pK* determinations of the acids. For a series of runs in which the concentration of buffer, including both phosphate and sulfite, was changed but the ratio of buffer salts and the total ionic strength were left constant, the pH did not vary more than ± 0.02 pH unit.

Bisulfite-Adduct Formation.—The equilibrium constants, *K*, were determined from the slope of a plot of

$$(D_M - D_C)/(D_Q - D_M) \text{ vs. } 1/(\text{HSO}_3^-)$$

where *D_Q*, *D_C*, and *D_M* are, respectively, the absorptions due to quinone, the quinone-bisulfite adduct, and the mixture of the two species at some HSO_3^- concentration. All three absorptions were read at the $\lambda_{D_{\max}}$ of the quinone; *D_C* could be measured under equilibrium conditions. For quinones with a labile substituent, the density continued to change when the bisulfite addition reaction was near completion because of the products formed in the displacement reactions. Fortunately, the latter was usually much slower, so *D_C* could be taken at a time when the addition reaction was at least 99% complete, but the displacement reactions were less than 2% complete.

Kinetics of Quinone-Bisulfite Adduct Formation. Preparation of Solutions.—For each kinetic run, a buffer solution was prepared by mixing appropriate volumes of KH_2PO_4 , K_2HPO_4 , and sodium bisulfite stock solutions to give a final ionic strength of 0.225 in the reaction solution. The sulfite-bisulfite amounted only to about 2% of the total ionic strength. In cases where the buffer ion was decreased, the ionic strength was maintained at 0.225 with potassium chloride.

Quinone solutions ($10^{-4} M$) were prepared by first dissolving the substrate in 1 to 4 ml. of ethyl alcohol and adding this solution to 1 l. of water, with rapid stirring.

Solutions of 2-sulfo-3,5,6-trimethyl-*p*-benzoquinone were prepared *in situ* by allowing equimolar quantities of 2-iodo-3,5,6-trimethyl-*p*-benzoquinone and sulfite at pH 7 to react for 1 hr. This very rapid displacement reaction was easily complete in that time, as evidenced by the change in absorption spectrum from the two peaks of the iodoquinone to one with a single strong absorption at 260 μ . Addition of more sulfite caused the density to decrease, but the $\lambda_{D_{\max}}$ remained practically constant (Table I). These spectral changes were similar to those occurring in other quinones under the same conditions, indicating that the same kind of reaction was taking place.

Measurements of Rates.—The reactions were started by mixing appropriate volumes of the buffer and quinone solutions.

For duroquinone, these solutions were mixed manually, transferred immediately into a Beckman quartz cell, and the top was sealed with stopcock grease to exclude air. The drop in absorption was followed at the $\lambda_{D_{\max}}$ of the quinone on a Beckman Model DU spectrophotometer with a hydrogen lamp as source.

The reaction rates of the bromo-, chloro-, and sulfotrimethyl-*p*-benzoquinones were followed on the mixing machine by the stop-flow method. The quinone and buffer solutions were brought together in a mixing chamber and passed through a

quartz cell. The flow into the cell was stopped at the same time the recorder was started and the drop in absorption at the $\lambda_{D_{\max}}$ of the quinone was recorded with time. For the sulfoquinone, this density after several minutes became constant, *i.e.*, the curve underwent no further change, and this density was taken as *D_C*. Since the bromo- and chloroquinones underwent a displacement reaction with sulfite, the absorption continued to change slowly even after several minutes. The kinetics were run at a low enough pH to keep the sulfite concentration low. Under these conditions, the addition reaction was still quite rapid and was complete when the displacement reaction was only 2% complete; *D_C* was taken after a calculated time (~ 2 -3 min.).

Kinetics of Displacement Reactions.—All displacement rates were run at an ionic strength of 0.065.

Iodide displacement reaction rates were followed on the mixing machine. Equal volumes of the buffer solution, containing phosphate and sulfite, and of the quinone solution (10^{-4} to $2.5 \times 10^{-4} M$), both kept under nitrogen, were brought together in the mixing chamber and passed through the quartz cell. Depending on the rate, either the steady-state method or the stopped-flow method was used to measure the drop in quinone absorption at 286 μ *vs.* time. In an alternative procedure, the quenched-flow method was used in which one volume of buffer solution was mixed with 3 volumes of quinone solution ($2.7 \times 10^{-4} M$) and allowed to flow through different spacers of known length at a constant rate. The reaction was quenched by lowering the pH to ~ 3 with dilute nitric acid. The iodide in these samples was titrated with 0.001 *M* silver nitrate, using eosin as indicator.⁴¹ The rate of disappearance of quinone by absorption was found to be equal to the rate of release of iodide ion as determined by titration.

Bromide displacement rates were followed by measuring the bromide concentration potentiometrically during the reaction with a Leeds and Northrup Model 3664 pH meter and a silver-silver bromide electrode, prepared from a polished silver billet electrode No. 39261. The reference electrode was a Beckman No. 39270 fiber-type calomel electrode, connected to an external potassium nitrate salt bridge.

A plot of potential *vs.* log bromide concentration was not linear in the presence of sulfite. Therefore, calibration curves were prepared for the concentrations of sulfite used. Known volumes of standardized potassium bromide were added to several reaction blanks containing all the components of the reaction mixture except quinone, and the potential was noted for each addition. Higher concentrations of sulfite and higher pH values produced greater deviations from linearity in the potential *vs.* log bromide concentration plot. The bromide concentrations were determined during the reaction from the potential using this plot. The calculated final bromide concentration always agreed with that obtained from the final potential using the calibration, indicating that the quinone did not interfere.

The reactions were run under nitrogen and were fast enough so that the temperature, adjusted to 25° , at the start, did not vary more than $\pm 0.1^\circ$. Reactions were started by adding sodium bisulfite stock solution to an aqueous quinone-potassium bromide solution. The initial quinone concentration was $4 \times 10^{-4} M$, and the sulfite and bisulfite concentrations are given in Table III. Potassium bromide ($4 \times 10^{-3} M$) was added to the reaction mixture so that the electrode would give a reliable reading at the start.

The use of large excesses of bisulfite (as well as of the buffer to maintain constant pH) facilitated the rate calculations, since the ratio Br^-/BrO^- was constant in each run under these conditions.

Chloride displacement rates were measured with a silver-silver chloride electrode by a modification of the method used for bromide displacement rates. Sulfite produced much greater deviations in the potential *vs.* log chloride concentration curves than in potential *vs.* log bromide concentration curves, so that reproducible results could only be obtained below pH 4. Reaction mixtures of the chloroquinone and sulfite were prepared as for the bromoquinone, but aliquots of these mixtures were quenched with dilute nitric acid to pH 3.5 before the potential was measured. The concentration of chloride ion was taken from a calibration curve previously prepared at this pH value.

Spectra of Products.—The spectra of the displacement products of the three halotrimethylquinones were identical under the same conditions above 250 μ . Below this wave length, sulfite and bisulfite and the halides absorbed strongly. When the three curves were corrected for these additional absorbances, they were seen to be identical down to 225 μ , which is the limit of the spectrophotometer.

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