Absorption Spectra.—The ultraviolet absorption spectra of the two polymorphic forms of isotenulin and of tenulin (Fig. 1) were determined in 95% alcohol with a Beckman spectrophotometer.[11] The concentration was 0.0000709 mole per liter.

The infrared spectra (Fig. 2) of isotenulin, m. p. 152.3–153.5°, and the sample of Dr. Adams were determined with a Beckman IR2 spectrophotometer as Nujol mulls in a 0.050-mm. cell against air as reference.[11] The spectra agreed in virtually every significant band.

The Action of Alkali on Isotenulin.—The pure compound (0.1 g.) (m. p. 152.3–153.3°) was dissolved in a solution of 10 cc. of 0.1247 N aqueous sodium hydroxide and 20 cc. of ethyl alcohol. The resulting solution was refluxed for one hour in an atmosphere of nitrogen. Titration with 0.1058 *N* hydrochloric acid against phenolphthalein showed a consumption of 2.09 moles of alkali. When an identical mixture was allowed to stand for twenty-four hours at room temperature, 1.7 moles of alkali was used.

Summary

The bitter principle of *Helenium tenuifolium*, tenulin, has been isolated from the dried plant by an improved method of extraction. It probably occurs in the plant together with the isomeric isotenulin.

Isotenulin contains besides the previously established acetoxyl group probably an α,β-unsaturated carbonyl group and a group which consumes one mole of alkali and is tentatively assigned a lactone structure.

COLUMBIA, MISSOURI

RECEIVED APRIL 12, 1948

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[11] Absorption spectra by Dr. E. E. Pickett, University of Missouri.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BENARES HINDU UNIVERSITY]

Production of *Joshi-Effect* in Bromine Vapor under Silent Electric Discharge

BY G. S. DESHMUKH AND S. SIRSIKAR

Previous work[1,2,3] reported occurrence of the above *effect* Δi an instantaneous and reversible photo-decrease of the discharge current i in chlorine, bromine, iodine, oxygen, air, nitrogen and hydrogen. Results[1,4,5,9,10] of detailed investigation in these laboratories in the case of the chlorine gas, in which Δi is apparently most pronounced and easiest to study, have shown that under favorable conditions, it can be as high as 93% current suppression employing but ordinary light.[4] Preliminary work[3] with the last six of the above gases showed that under arbitrary conditions Δi varied from 7% in bromine vapor to about 0.1% in hydrogen. Using improved technique and Joshi's deduction[5,6,7,8] of the maximizing influence on Δi of the gas pressure, excitation near "threshold potential," and a moderately low temperature, the present work has revealed that remarkably enough, the *Joshi-effect* in bromine vapor reaches almost a 100% current decrease (*vide infra*).

Experimental

The general experimental procedure and apparatus used were essentially the same as described elsewhere.[3] Bromine vapor purified carefully by fractionation over liquid air, and freed from uncondensable impurities by pumping off with a Töpler, was frozen in a small bulb sealed serially with the annular space of a Siemens type (glass) ozonizer (Fig. 1). The amount of bromine introduced in the system was such that at even the highest temperature (about 75°) employed during these experiments, some liquid phase remained. The bromine (vapor) pressures for these temperatures were obtained by interpolation from a log *p–t* curve, using Ramsay and Young's data[11] (*cf.* inset curve A, Fig. 3).

Joshi[1,6,7] has shown that relatively, Δi may be enhanced by increasing the area of the excited surface. A large size ozonizer (about 100 cm. long and 4 cm. in diameter) was therefore, employed. This proved to be a marked advantage in increasing greatly the magnitude of Δi compared with earlier results[2,3]; also, it enabled a study over a wider range of exciting potentials, the general influence of the gas pressure and temperature on the production of Δi considered in Joshi's theory.[8]

The ozonizer was surrounded by a large-size glass jacket filled with water (Fig. 1); this served to reduce any temperature fluctuations during a given series of observations and also minimize any heating effects due to the discharge; and irradiation used for the production of Δi. The entire system was enclosed in an electrically heated asbestos chamber (Fig. 1). It had a glass window of about the ozonizer size fitted with an asbestos shutter worked by a pulley. The inner tube of the ozonizer filled with salt solution and forming one electrode, was connected through a 20,000-ohm Dubilier type stabilizing resistance to one of the secondaries of a H.T. transformer; its other terminal was earthed. The outer electrode of the ozonizer (L.T. in Fig. 1) formed with salt solution was also earthed through a Cambridge a.c. microammeter (μ_A in Fig. 1) of the double wave, metal oxide, rectifier type, which served to measure the

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(1) Joshi, Presi. Addr. Chem. Sec., Indian Sci. Cong. (1943).

(2) Joshi and Deshmukh, *Nature*, **147**, 806 (1941).

(3) Deshmukh, *J. Indian Chem. Soc.*, **24**, 211 (1947).

(4) Joshi and Deo, *Nature*, **153**, 434 (1944).

(5) Joshi, *Proc. Indian Acad. Sci.*, **A22**, 225, 293, 389 (1945).

(6) Joshi, *Curr. Sci.*, **15**, 281 (1946); **8**, 548 (1939).

(7) Joshi, *ibid.*, **16**, 19–21 (1947).

(8) Joshi, *Proc. Indian Sci. Cong., Phys. Sec.*, Abst. 26 (1946); *ibid.* (1947).

(9) Deo, *Proc. Indian Acad. Sci.*, **A21**, 76 (1945).

(10) Joshi, *Nature*, **154**, 147 (1944).

(11) *Cf.* Kaye and Laby, "Physical and Chemical Constants," Longmans, 1936, p. 44.

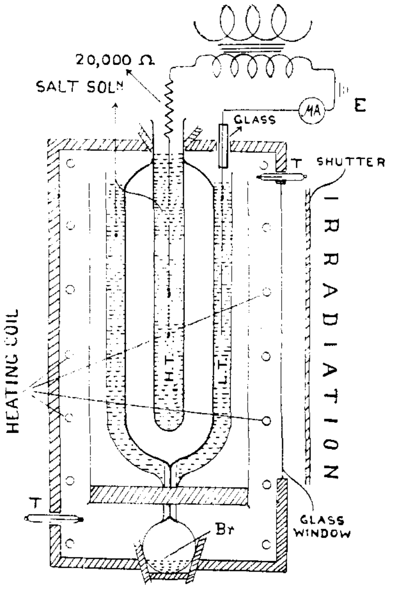

Fig. 1.—Apparatus for production of Joshi-effect in bromine vapor in silent discharge.

discharge current i. The primary of the transformer was fed with the a.c. output from a rotary converter worked off 220 volt, d.c. mains. The potential applied to the ozonizer V, expressed in kilovolts (r.m.s.) and denoted by kV, was maintained constant within one per cent. by hand regulation of a variable resistance introduced in the primary of the transformer. The Joshi-effect Δi was studied under irradiation from a 220-volt, 200-watt incandescent (glass) bulb. The discharge current flowing through the ozonizer at a given applied potential V in dark, i_D, was observed with the external light on, and the glass window closed with the shutter; the corresponding current under irradiation, i_L, was next noted, when the shutter was raised. $i_D - i_L = \Delta i$ gives the net Joshi-effect; the corresponding relative value suited for purposes of comparison is $100\ \Delta i/i_D = \%\Delta i$.

Before commencing any series of V–i observations (*cf.* Figs. 2–4), the constancy of the temperature of the system over an appreciable time period was ensured by adjusting the heating current. The time for observing i_D and i_L was thirty seconds in all cases, the applied potential V being kept constant at the desired value. The discharge was then switched off and the system allowed to stand over for fifteen minutes, the temperature being kept constant. The applied kV. was next raised to a higher value and the corresponding i_D and i_L determined within thirty seconds, and so on. The above restriction of the time of exposure to discharge served to minimize any current change due to "aging,"[1,2,9] *i. e.*, a time-variation of the current at a constant V. (This "aging" effect was sensible in the present arrangement only at large V, *e. g.*, above 6.4 kV.)

The main curves in Figs. 2 and 3 represent the V–i characteristics in dark and light; and the corresponding Δi and $\%\ \Delta i$; at 5° and 23°, respectively, in the range 1 to 8 kV. Similar data for 50, 60, 75° and when the bromine bulb was cooled by liquid air are shown in Fig. 4. Table I gives the above quantities, being read off from (smooth) curves in Figs. 2–4.

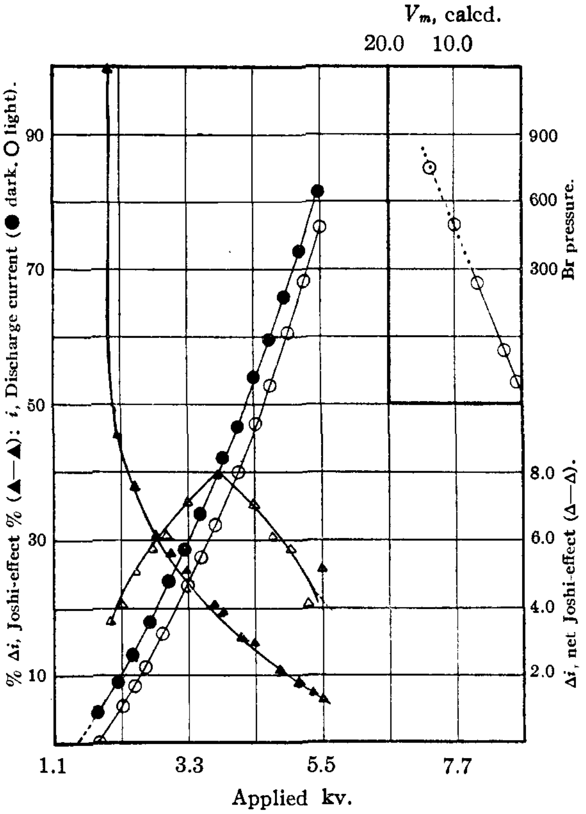

Fig. 2.

The approximate minimum potential $V_{\bar{m}}$ at which at a given temperature Δi was detected, was noted from the V–i characteristic at that temperature. The corresponding bromine pressures obtained from curve A in Fig. 3 are plotted against $V_{\bar{m}}$ in Fig. 2; other curves in Fig. 3 are explained later.

Results and Discussion

The data in Figs. 2–4 illustrate the applicability to bromine vapor of a general result, observed by Joshi to be a characteristic of this phenomenon. It is that Δi is produced above V_m the "threshold potential" where the gas breaks down as a dielectric; V_m is characterized by a rapid rise of current i with the applied potential V. The results also show that at a constant temperature, the net effect Δi increases by increasing V; the corresponding relative effect $\%\ \Delta i$, however, decreases. At much larger V (or rather, $V - V_m$), even Δi decreases (Figs. 2 and 3). The influence of temperature over 5° to 75° on the conductivity in dark i_D and the relative effect $\%\ \Delta i$ in bromine vapor at

TABLE I

INFLUENCE OF TEMPERATURE AND EXCITING POTENTIAL ON JOSHI-EFFECT IN BROMINE VAPOR

	50°C.				23°C.				50°C.				60°C.		75°C.		Br bulb cooled by liquid air	
kV	i_D	i_L	Δi	$\% \Delta i$	i_D	i_L	Δi	$\% \Delta i$	i_D	i_L	Δi	$\% \Delta i$	i_D	i_L	i_D	i_L	i_D	i_L
1.8	3.5	..	3.5	100	..	..	...	..	..	..	...	..	..	...	...	...	...	...
2.2	8.5	4.5	4.0	47	..	..	...	..	..	..	...	..	...	...	...	...	...	...
3.3	28.5	21.5	7.0	25	6.5	3.5	3.0	44	..	..	...	..	...	...	...	...	...	...
4.4	53.5	46.5	7.0	13	24.5	17.5	7.0	29	..	..	...	..	...	...	...	...	...	...
5.5	80.0	75.0	5.0	6	46.5	37.5	9.0	19	..	..	...	..	...	...	...	...	...	...
6.7	..	..	...	...	84.5	76.5	8.0	9.5	2.5	2.5	...	..	1.5	1.5	1.5	1.5	2.0	2.0
7.6	..	..	...	...	..	..	...	..	6.5	5.5	1.0	15	2.5	2.5	2.5	2.5	3.0	3.0
8.2	..	..	...	...	..	..	...	..	13.5	11.5	2.0	15	5.5	5.5	3.5	3.5	3.5	3.5

3.3, 4.4, 5.5, 6.7 and 8.2 kV. is shown graphically in the inset in Fig. 3, employing values read off from the appropriate *V–i* characteristics in Figs. 2–4. It is seen that at a constant applied *V*, i_D

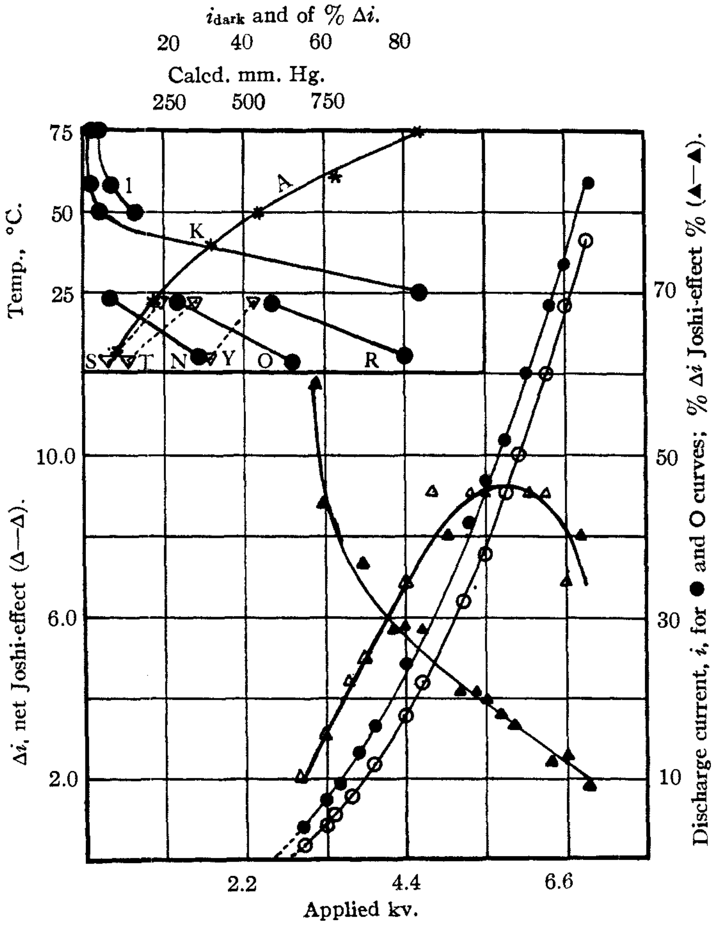

Fig. 3.—Joshi-effect in bromine vapor in electric discharge at 23°: upper curves, i_{dark} ●, I 8.2, K 6.7, R 5.5, O 4.4, N 3.3 kv.; A * bromine pressure; Δ, % Δ*i*, S 3.3, T 4.4, Y 5.5 kv. Lower curves: ●, i_{dark}; O, i_{light}; Δ, Δ*i*; ▲, % Δ*i*.

decreases and % Δ*i* increases with the rise of temperature. Thus, *e.g.*, at 3.3 kV., i_D at 5° and 23° is about 28 and 6 μa., respectively; the corresponding % Δ*i*, however, increases from 25 to 44. Under the operative conditions described already, the mass and, therefore, the pressure of bromine vapor in the discharge space increases rapidly with temperature, as shown by curve A in Fig. 3. The much reduced conductivity i_D at a constant *V* and higher temperatures follows, therefore, from the increase with pressure of the "threshold potential" V_m and Joshi's general result that *i* depends on $V - V_m$.[6,5,7,8,12] Earlier results[4] in these laboratories especially in the case of the chlorine gas have shown (a) that at a constant temperature and applied *V*, within limits, % Δ*i* increases by increasing *p*; and (b) that at a given *V*, with a constant mass of the excited gas, increase of temperature reduces % Δ*i*. This applies also to % Δ*i* in iodine, oxygen and mercury vapor, now being studied in these laboratories. The observed increase with temperature of % Δ*i* suggests by analogy with the chlorine results[4] that the possibly adverse effect of temperature *per se* on % Δ*i* in bromine, is more than compensated by its increased pressure. Besides this, the comparatively marked reduction in % Δ*i* at a constant applied *V* and low temperature (shown by broken % Δ*i* – *t*° curves for 3.3, 4.4 and 5.5 kV. in the inset in Fig. 3) may be attributed to the (not entirely independent) circumstance that at reduced *p* due to cooling, i_D increases more sharply than Δ*i* as illustrated by results at 5, 23 and 50° (*cf.* also Table I, Figs. 2–4).

The non-occurrence of Δ*i* at 60° and 75° (*cf.* Fig. 4) is explicable on following considerations due to Joshi.[6,10,12] The production of Δ*i*, like any other discharge reaction, should set in above its characteristic potential, say $V_{\bar{m}}$; for bromine vapor under conditions employed in this work, especially at low temperatures, $V_{\bar{m}}$ is

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(12) Joshi and Deshmukh, *Nature*, **155**, 483 (1945).

apparently close to the "threshold potential" V_m (*vide supra*). Between V_m and $V_{\overline{m}}$, there is current, but not Δi. Like the Paschen potential, V_m in especially ozonizer discharges increases almost linearly with the gas pressure. As deduced from the characteristic V–i curves in dark and light, the potential $V_{\overline{m}}$ where the Joshi-effect Δi sets in, increases smoothly with increasing pressure (*cf.* inset curve at top of Fig. 2). At 5, 23 and 50° (*i. e.*, 80, 200 and 560 mm. bromine pressures), $V_{\overline{m}}$ is about 1.8, 3 and 7.3 kV. respectively; the temperature 60 and 75° correspond to 790 and 1050 mm. and to 10 and 13 kV. for $V_{\overline{m}}$, as judged by extrapolation from the curve in Fig. 2. The non-occurrence of Δi at even the largest applied potential, *viz.*, 8.2 kv., is therefore explicable. The adverse influence of temperature on Δi by analogy with results in other systems and anticipated from Joshi's theory[6,7,8] (*vide infra*) is another limiting factor.

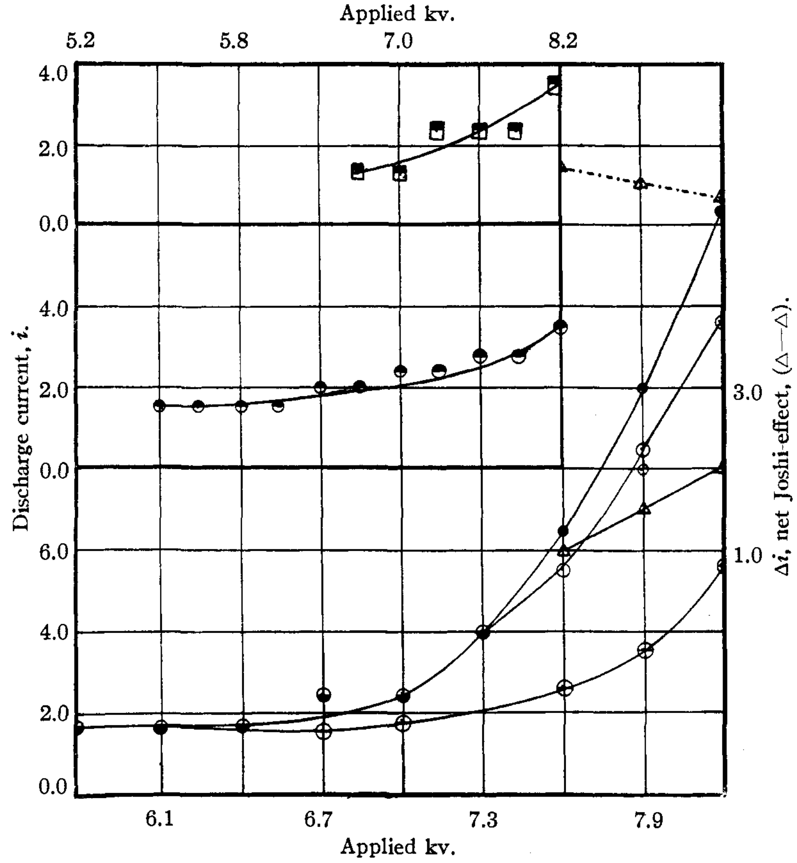

Fig. 4.—Joshi-effect in bromine vapor in electric discharge at 50, 60 and 75°: top, ▣, 75°, dark–light; middle, ⊖, bromine bulb cooled by liquid air. For the lower curves: at 50°, Δ-·-Δ, % Δi; Δ—Δ, Δi; ●, i_{dark}; ○, i_{light}; ⊕, dark–light at 60°.

The absence of Δi on cooling the bromine bulb by liquid air (*cf.* Fig. 4) despite a wide variation of the applied V, is attributable to the negligibly small pressure of bromine vapor, a deduction borne out by like results in chlorine[4] and other gases. A consideration of the various V–i curves in dark and light in Figs. 2–4 suggests that at a given p and temperature, % Δi reaches a maximum as the applied potential V equals the "threshold potential" V_m (*under light*); the corresponding discharge current is then suppressed almost completely on irradiating the system. Thus, *e. g.*, the curves in Fig. 2 show that at 5° when the exciting potential V is 1.8 kV. (which also corresponds to V_m *in light*) the current under light, i_L, is negligibly small and % Δi is practically 100. This is also suggested by results at the next higher temperature, *viz.*, 23° as shown in Fig. 3. The curve for i_L cuts the voltage axis at about 2.7 kV., which corresponds to V_m *under light.* At this applied potential % Δi is markedly high. That as a general result, *excitation at* V_m *under light* should maximize % Δi independent of pressure, temperature and nature of the excited gas is now being investigated.

Joshi[6,7,8] has suggested that an adsorption-like boundary layer from the ions and molecules of the excited gas is the chief seat of Δi. Electrons, released from this layer under light are captured by the excited gas particles, owing to their electron affinity; these then give slow moving negative ions and produce the decrease Δi as a space charge effect. Since the probability of electron capture by an atom depends on p/E, where E is the electrical field, the observed influence of V in reducing % Δi follows[7,8]; its decrease on heating is attributed to the corresponding deformation of the boundary layer. That *ceteris paribus*, the order of % Δi in various gases and vapors follows that for their electron affinity; and that within limits a pressure rise increases % Δi follows from the above mechanism.[7,8] This Δi phenomenon may be related to the Budde-effect, a reversible photo-expansion observed in neutral chlorine and bromine. Joshi-effect is, however, more widespread and shows a much greater magnitude than the Budde-effect, presumably because of the greater concentration of the excited particles produced under the discharge, prior to irradiation.

Our grateful thanks are due to Professor S. S. Joshi, D.Sc. (London), F.N.I., for suggesting the problem, advice and guidance during the work.

Summary

Production of Joshi-effect, an (almost) instantaneous and reversible photo-decrease Δi of the

discharge current i at an applied potential V is studied in bromine vapor over the temperature range 5 to 75°. A large-size Siemens type ozonizer energized by 1 to 8 kilovolts of 50 cycles frequency was used. At a given temperature, the net effect Δi increases with V; the corresponding relative effect $\% \Delta i$, however, decreases rapidly. At large V, Δi also decreases with V. Within limits, increase of pressure and reduction of temperature increase $\% \ \Delta i$. When excited at a low temperature and near the "threshold potential," the discharge current became negligible when exposed to ordinary light. The results are in agreement with Joshi's theory, which regards that an activated, adsorption-like, wall layer formed with ions and molecules of the gas is the chief seat of the effect Δi; light releases photo-electrons from this layer which owing to the electron affinity of the excited atoms, are captured by them to form slow moving negative ions and cause the decrease Δi as a space charge effect.

BENARES, INDIA RECEIVED APRIL 25, 1948

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Catalysis by Manganic Ion of the Reaction of Bromine and Oxalic Acid. Stability of Manganic Ion Complexes

BY HENRY TAUBE

Earlier work[1a] on the reduction of manganic ion by oxalate demonstrated the important role played in the kinetics of the process by the formation of complexes between manganic ion and oxalate ion. The existence of such complexes also in media at very low oxalate ion concentration and their significance in the electron transfer process was demonstrated in an investigation of the manganic ion catalyzed reaction between chlorine and oxalic acid.[2]

A result of especial interest exposed in the catalytic work was that the initial rate of the catalyzed chlorine–oxalic reaction is independent of the concentration of chlorine. It depends only on the rate of interaction of manganic ion and oxalate, and the observed kinetics pointed to the decomposition of the complex ion $MnC_2O_4^+$ as the principal rate-determining step. The conclusion that the interaction of manganic ion and oxalate alone determines the initial rate of the catalyzed reaction was confirmed by the quantitative agreement observed for the rates of the direct and catalyzed reactions.[1b] It seemed of interest to extend the catalytic work, investigating the catalytic effect of manganic ion on the reaction with oxalic acid of oxidizing agents other than chlorine, particularly since quantitative agreement of initial rates with those observed in the catalyzed chlorine–oxalic acid reaction would further substantiate certain of the conclusions about mechanism. In the present paper the results obtained in a study of the reaction of bromine and oxalic acid

$$H_2C_2O_4 + Br_2 = 2H^+ + 2Br^- + 2CO_2$$

catalyzed by manganic ion are presented and discussed.

For the purpose of direct comparison with the earlier work, in some of the experiments the reaction medium was a solution 2 M in hydrochloric acid. Most of the results, however, were obtained using perchloric acid as the strong mineral acid. These results are of particular importance because the difficulty due to the unknown extent of complex ion formation between manganic ion and the halide ion is avoided in the experiments with perchloric acid. The chlorine–oxalic acid system required a reaction medium high in hydrochloric acid to reduce the rate of the spontaneous reaction sufficiently, but in the present system, at high hydrogen ion concentration, the rate of the spontaneous reaction remains small even when the concentration of bromide ion is as low as 0.001 M.

In most respects, the effects observed in the system under present study are similar to those noted in the chlorine–oxalic work. Thus, the kinetic behavior considering initial rates for the catalyzed reaction of bromine and oxalic acid in 2 M hydrochloric acid is the same as for the reaction between chlorine and oxalic acid under the same conditions, and, in fact, the specific rates for the two systems are identical within the limits of experimental error. When the reaction medium is 2 M perchloric acid, the form of the rate law with respect to the dependence of initial rate on the concentration of bromine, oxalic acid and manganic ion is unchanged, and the specific rates at moderate and high values of oxalic acid agree fairly closely with those obtained in 2 M hydrochloric acid.

The data obtained with perchloric acid as the reaction medium have yielded some new conclusions. From the results of the experiments for low concentrations of oxalic acid a value for the constant governing the association of oxalate and the uncomplexed (except by water or OH^-) manganic ion has been calculated. Further experiments, with chloride ion and other complexing anions added, have yielded information about the association also of these anions with manganic ion.

Over wide ranges of the concentrations of the

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(1) (a) Launer, THIS JOURNAL, **54**, 2597 (1932); Duke, *ibid.*, **69**, 2885 (1947); (b) Taube, *ibid.*, **70**, 1216 (1948).

(2) Taube, *ibid.*, **69**, 1418 (1947).