ings" of the X-ray photograph, very useful for identification of phases.

Both beta and gamma curd phases are destroyed upon heating to nearly 100°. They are transformed into supercurd. For sodium stearate, dilatometric[8] and X-ray patterns show that the gamma phase is converted into supercurd at the first order transition point 89°, whereas the heat change shown by calorimetry[9] gave the value 90°. Upon cooling to room temperature gamma phase is reformed. Indeed, gamma phase is reformed at room temperature upon subsequent cooling, no matter how high the sodium stearate is heated, through the waxy and anisotropic liquid forms up to final melting to isotropic liquid above 288°.

General Conclusion

All crystals of soap consist of layers of double molecules placed end to end, hydrocarbon to hydrocarbon and carboxyl group to carboxyl group. As a first approximation c is the double length of the molecule, b is twice the thickness of the molecule and a is twice the width of the molecule in the plane of the hydrocarbon zig-zag chain. The different crystalline forms differ chiefly in the angle of tilt of the molecule, and in minor details of close packing in the a and b directions. Water lengthens the $c \sin \beta$ spacing, presumably by entering amongst and between the polar heads. Even the alpha form has been shown by Buerger[10] to be not strictly orthorhombic but to possess a slight monoclinic inclination. If the successive layers of double molecules do not fit exactly end to end but are staggered alternately, the unit cell naturally has to be doubled, as was shown for the special case of Buerger's crystal. Such modifications do not essentially alter the first statement of this paragraph. We therefore have a direct physical significance for the 001 spacing as being approximately $\sin \beta$ times the double length of the molecule, 020 being the thickness of the molecule and 200 approximately equal to $\sin \beta$ times the width of the zig-zag hydrocarbon chains.

Summary

Fiber as well as powder photographs of sodium laurate, palmitate and stearate have been made. They confirm the unit cell of the beta form of monoclinic soap and give the unit cell for a "hydrated gamma form" of monoclinic soap at room temperature.

Alpha, beta and gamma forms differ primarily in long spacings, but likewise to a lesser extent in the lines corresponding to side spacings. The strongest characteristic beta line in the powder diagram corresponds to $d/n = 4.28$ Å., whereas that of the hydrated gamma or gamma phase is $d/n = 4.00$ Å.

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED FEBRUARY 8, 1943

---

[8] M. J. Vold, M. Macomber and R. D. Vold, THIS JOURNAL, 63, 168 (1941).

[9] R. D. Vold, *ibid.*, 63, 2915 (1941).

[10] M. J. Buerger, *Proc. Nat. Acad. Sci.*, 28, 529 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Induced Chlorination of Maleic Acid. Evidence for Chain Reaction Mechanisms

BY HENRY TAUBE

The results to be presented show that certain substances when added to a solution containing maleic acid, chlorine and hydrochloric acid, induce the addition of chlorine to maleic acid. It is observed that the induction factor can rise to large values (exceeding 200 in some cases) and that the effect continues only while the inductor is being consumed. Among the substances which induce the reaction are Fe^{++} and Ti^{+++}; it is assumed that these and other reducing agents which produce the effect, do so because they reduce chlorine by a one-electron change to produce atomic chlorine[1] in the first step as shown by the equation below for ferrous ion.

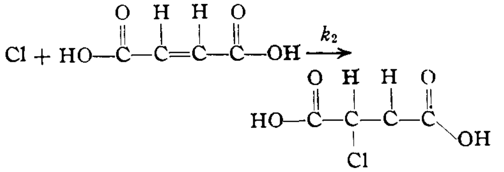
$$Fe^{++} + Cl_2 \longrightarrow FeCl^{++} + Cl \qquad (1)$$

Atomic chlorine can set up a chain reaction of the type[2]

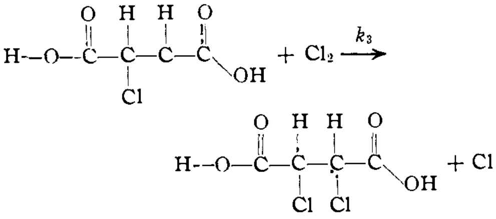
---

[1] The substance present as the reactive intermediate in solutions of the chloride ion concentration employed is probably Cl_2^- (Taube and Bray, THIS JOURNAL, 62, 3369 (1940)). For convenience in representing reactions, the simple formula Cl is employed throughout.

[2] Similar mechanisms are proposed for the photo addition of halogens to certain substances containing double bonds: Rollefson and Burton, "Photochemistry," Prentice-Hall, New York, N. Y., 1942.

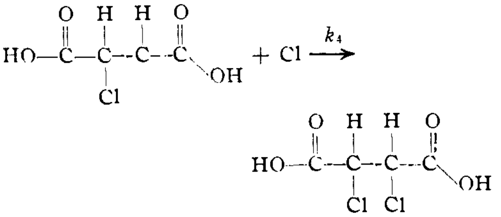


$$\mathrm{Cl} + \mathrm{HO{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}{=}\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{OH} \xrightarrow{k_2} \mathrm{HO{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}{-}\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{\diagdown}\mathrm{OH} \qquad (2)$$



$$\mathrm{H{-}O{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}{-}\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{\diagdown}\mathrm{OH} + \mathrm{Cl_2} \xrightarrow{k_3} \mathrm{H{-}O{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}{-}\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{\diagdown}\mathrm{OH} + \mathrm{Cl} \qquad (3)$$

As chain breaking steps reactions (4) and (5) operate, reaction (4) predominating at low values of the ratio of chlorine to maleic acid and (5) at high values of this ratio.



$$\mathrm{HO{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}{-}\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{\diagdown}\mathrm{OH} + \mathrm{Cl} \xrightarrow{k_4} \mathrm{HO{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}{-}\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{\diagdown}\mathrm{OH} \qquad (4)$$

$$\mathrm{Cl} + \mathrm{Cl} \xrightarrow{k_5} \mathrm{Cl_2} \qquad (5)$$

The kinetics of the reaction have been studied over a wide range of conditions and are consistent with this mechanism. Experiments with inhibitors, and qualitative experiments on the corresponding photo reaction also support the mechanism.

Methods

Known volumes of hydrochloric acid and maleic acid solution were introduced into a blackened cell of the type shown in Fig. 1, and a current of carbon dioxide was passed through. After about forty minutes a measured volume of saturated chlorine solution was added, the buret containing the inductor put in place, and the inductor allowed to flow in at a known constant rate, with violent stirring of the solution in the cell. The cell content was then introduced below the surface of potassium iodide solution and the liberated iodine titrated. The initial concentration of the chlorine was determined by running a volume of the saturated solution equal to that added to the cell into potassium iodide solution and again titrating the iodine. The difference in the values, corrected for the uninduced reaction of chlorine with maleic acid, and for accidental loss, measures the extent of the induced reaction. The correction mentioned above amounted in general to between 5 and 10% of the total decrease in chlorine, and was shown by repeated blank experiments to be reproducible. The time of addition of the inductor was usually of the order of five to ten seconds, and the chlorine and maleic acid were in contact about a minute before quenching.

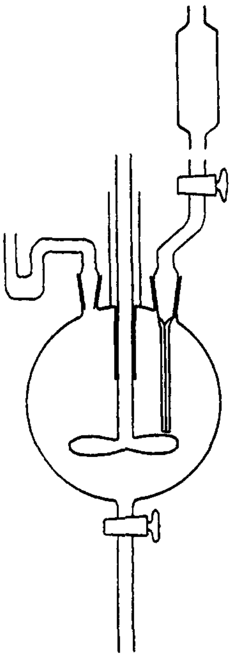


Fig. 1.—The entry at the right was used to introduce the solutions and the current of carbon dioxide. The tube at the left contained potassium iodide solution, which served to trap chlorine.

To eliminate the inhibitory effect of oxygen on the induced reaction, carbon dioxide was passed through the inductor solution, and the pipet (which was fitted with a large bulb above the calibration mark) was swept free of air by carbon dioxide. A current of carbon dioxide was also swept through the tube surrounding the stirrer.

The volume of the inductor solution added was in general only 3 to 5% of the total volume of liquid. Volumes of the solution were so chosen that after the addition of the inductor, the gas volume in the cell was about 3 cc.

It was proved by an experiment in which a relatively large quantity of chlorine was consumed by the induced reaction with maleic acid that there is no appreciable change in acidity during the reaction and it was concluded that the amount of chlorine consumed by addition of hypochlorous acid, or by substitution of hydrogen atoms, amounted to less than 2% of the total for the conditions of the experiments. In order to determine whether the main product is meso or racemic dichlorosuccinic acid, the reaction mixture was extracted with ether and the ether extract evaporated. The material left was dissolved in alcohol and the melting (decomposition) temperatures of succeeding fractions taken. The first quarter melted at a temperature of about 218°, which corresponds to the melting point of *meso*-dichlorosuccinic acid[3]; the third quarter also melted at this temperature, although there was evidence of some change in the solid before it melted. This change—loss of material by volatilization—was due mainly to the impurity, maleic acid (the reaction mixture contained maleic acid in excess). It is concluded that the main product of the reaction is *meso*-dichlorosuccinic acid.[3] No appreciable amount of fumaric acid could be detected as product. An experiment also showed that the photochemical chlorination under similar conditions also gave mainly *meso*-dichlorosuccinic acid as product, with no appreciable production of fumaric acid.

Materials.—Redistilled water was used as the solvent. Chlorine and carbon dioxide were tank quality. The maleic acid solutions were obtained by dissolving redistilled C. P. maleic anhydride in water. For experiments at low concentrations of chlorine, it was found necessary to photochlorinate the maleic acid to the extent of about 1%

---

(3) The non-induced reaction also yields *meso*-dichlorosuccinic acid as product at sufficiently high concentration of hydrogen ion and chloride ion; Terry and Eichelberger, THIS JOURNAL, **47**, 1067 (1925).

in order to eliminate an effect which gave specific reaction rates about 10% too high in the initial stages of the induced reaction. Further chlorination to the same extent had no appreciable effect on the specific rate.

Other chemicals were C. P. quality used without further purification.

Solutions of V^{++}, V^{+++}, Mo^{+3} (green and red forms), Mo^{+5} (brown) were obtained by electrolytic reduction of the higher valence states in hydrochloric acid solution. A solution containing Ti^{++} was prepared by the method of von der Pfordten.[4]

Conditions.—In all experiments on the induced reaction the ionic strength was 1.0, and in most cases the concentration of hydrochloric acid 1 *M*. In all cases, the maleic acid concentration was considerably in excess of the chlorine concentration, and the average value of the maleic acid concentration was used in the calculations.

The average value of total maleate (maleic acid + maleate ion) concentration is represented throughout by the symbol $(\overline{H_2M})$. The temperature was kept at 25.0°. The units employed are: concentration in moles per liter and time, *t*, in minutes.

Experiments and Discussion

The Uninduced Reaction.—Since chlorine adds to maleic acid at an appreciable rate also in the absence of inductors, some experiments on the rate of the uninduced reaction were performed. The results of this study are presented in Table I. The specific reaction rate *k* is defined by

$$-\frac{d(Cl_2)}{dt} = \frac{k(\text{maleic acid})(Cl_2)}{(H^+)}$$

TABLE I

THE RATE OF REACTION OF CHLORINE AND MALEIC ACID IN THE ABSENCE OF INDUCTORS

Temp. = 25°; μ = 0.6 except in Expt. 9 where it is 1.0.

No.	t	$(\overline{H_2M})$	$(Cl_2)_0 \times 10^2$	$(Cl_2)_t \times 10^2$	(HCl)	$k \times 10^2$	(H^+)
1[a]	5	0.197	0.9880	0.3776	0.10	6.25	0.127
2	5	.197	.9460	.3626	.10	6.22	.127
3	5	.199	.9014	.6171	.30	5.45	.311
4	10	.199	.8968	.6048	.60	5.38	.606
5	12	.095	1.025	.8230	.60	5.20	.603
6	6	.299	0.9484	.6745	.60	5.18	.609
7	7	.197	2.017	1.519	.60	5.60	.606
8	10	.200	0.1804	0.1215	.60	5.35	.606
9	10	.171	1.145	.9320	1.00	5.22	1.002

[a] Potassium nitrate instead of potassium chloride was added to raise μ to the value of 0.6.

and was calculated from the integrated form of the equation. The concentrations of maleic acid and of (H^+) were calculated from the amounts of maleic acid and hydrochloric acid added, using a value of 0.0178 for the dissociation constant of maleic acid at $\mu = 0.6$[5]; the same value was used for the single experiment at $\mu = 1.0$. The results tabulated show that the function[6] describes the rate of reaction over the range of variables studied, except for an increase at low values of (H^+).

The uninduced reaction is not affected by oxygen or other substances which inhibit the induced reaction and one may conclude from this that different mechanisms operate in the two cases.

The Induced Reaction.—The data on the induced reaction will be discussed, as presented, from the point of view of the mechanism suggested in the introduction. The values for (Cl_2) presented in the following tables for the induced reaction have been corrected for the accidental loss, and the uninduced reaction.

Table II presents the data for the range of low values of the ratio $(Cl_2)/(\overline{H_2M})$.

TABLE II

THE KINETICS OF THE INDUCED REACTION AT LOW VALUES OF $(Cl_2)/(\overline{H_2M})$

(HCl) = 1 *M*, μ = 1.0, *t* = 25°. *A* is the amount of Fe^{++} added (moles per liter of solution), *R* is the rate of addition of Fe^{++} (moles per liter per minute).

No.	$(\overline{H_2M})$	$(Cl_2)_0 \times 10^2$	$(Cl_2)_1 \times 10^2$	$A \times 10^5$	$R \times 10^4$	Chain[b] length	$\sqrt{k_2k_3/k_4}$
1	0.195	0.1384	0.0513	2.21	3.45	39	27.7
2	.195	.3760	.2005	2.66	3.45	66	26.2
3	.196	.7707	.6157	1.66	3.50	96	23.8
4	.194	.5907	.3797	2.77	3.45	76	23.4
5	.191	.6025	.2038	5.92	3.35	67	23.0
6	.193	1.413	1.018	3.90	3.40	102	19.4
7	.099	0.3513	0.1868	4.14	3.40	39	22.8
8	.600	.3323	.1325	1.96	3.48	102	26.2
9	.194	.7081	.4234	7.06	14.0	40	23.0
10	.193	.6517	.4148	1.98	1.36	120	21.6
11	.191	.6961	.5972	0.825	0.33	120	9.7
12[a]	.390	.6451	.3575	2.81	3.88	102	23.0

[a] In expt. 12, the inductor was Ce^{+4}; this experiment will be discussed in connection with the data of Table III. [b] The chain length is defined as $\Delta(Cl_2)/A$ and is equal to the "induction factor" as used in the introduction. The values of (Cl_2) tabulated have been corrected for the I_2 liberated by Fe^{+++} in the determination of Cl_2. The correction is unimportant except for the experiments in which the chain length is small.

The differential equation for the chain reaction

$$\frac{-d(Cl_2)}{dt} = \sqrt{\frac{k_2k_3}{k_4}}\sqrt{(\overline{H_2M})\ (Cl_2)}$$

is derived from a mechanism which consists of reactions (1), (2), (3) and the chain breaking step (4). *R*, the rate of addition of the ferrous ion in moles per liter per minute, was set equal to the rate of chain initiation.[7] On integration, the

---

[4] Von der Pfordten, *Ann.*, **237**, 217 (1887).

[5] Taube, THIS JOURNAL, **65**, 526 (1943).

[6] A similar rate law is observed for the addition of bromine to maleic acid in aqueous solution. Bruner and Krolikowsky, *Bull. inter. Acad. Sciences, Krakow*, A, 192 (1910).

[7] The reaction between chlorine and ferrous ion is known to be exceedingly rapid and no after effects were observed in the experiments. Other inductors (Ti^{+++} and V^{+++}) show effects at low chlorine concentrations which can be explained if under such conditions, these inductors are not oxidized as rapidly as added, and the

function

$$\sqrt{\frac{k_2k_3}{k_4}} = \frac{2[\sqrt{(\mathrm{Cl_2})_0} - \sqrt{(\mathrm{Cl_2})_t}]\sqrt{R}}{A\sqrt{(\overline{\mathrm{H_2M}})}}$$

is obtained. The time $t = A/R$. Except for two trends, the function represents the data with reasonable fidelity over a wide range of maleic acid and chlorine concentrations, and of rate of addition of the inductor.

One of the trends, the marked falling off observed for $\sqrt{k_2k_3/k_4}$ as R is greatly decreased cannot be explained on the basis of experiments so far performed. Several explanations, consistent with (but not predicted by) the mechanism may account for it. One of these is that at low rates of free radical production, and therefore low values of the stationary concentration, a reaction which is first order with respect to free radical concentration becomes important as a chain breaking step.

The second trend, the decrease in $\sqrt{k_2k_3/k_4}$ as $(\mathrm{Cl_2})$ increases (or $(\overline{\mathrm{H_2M}})$ decreases, *cf.* expts. (2), (7) and (8)), is explained by the mechanism.

$$\text{Since: } \frac{(\mathrm{Cl})}{(\mathrm{H_2MCl})} = \frac{k_3}{k_2}\,\frac{(\mathrm{Cl_2})}{(\overline{\mathrm{H_2M}})}$$

it is expected that as the ratio $(\mathrm{Cl_2})/(\overline{\mathrm{H_2M}})$ increases, the stationary concentration of chlorine atoms will increase relative to that of the organic free radical $\mathrm{H_2MCl}$. On the basis of such considerations,[8] we would thus expect the chain breaking step (5) to become important as the ratio of $(\mathrm{Cl_2})/(\overline{\mathrm{H_2M}})$ increases, and in fact to predominate at sufficiently high values of this ratio. This accounts for the observed decrease in the values of $\sqrt{k_2k_3/k_4}$ as $(\mathrm{Cl_2})/(\overline{\mathrm{H_2M}})$ increases, and for the fact to be demonstrated in Table III, that at high values the mechanism consisting of reactions (1), (2), (3) and (5) describes the results.

Comparison of experiments (3), (4) and (5) shows that there is no serious trend of $\sqrt{k_2k_3/k_4}$ as the amount of added inductor is increased. This shows that initial effects have been eliminated, and that the products exert no appreciable effect. A two-fold increase in the rate of stirring did not affect the results, but a decrease by the same factor reduced the values of $\sqrt{k_2k_3/k_4}$ by about 5%. It can be concluded that the results as reported are substantially independent of stirring rate, and that the $\mathrm{Fe^{++}}$ is uniformly distributed throughout the liquid before it reacts.

Table III presents data for the region of higher values of $(\mathrm{Cl_2})/(\overline{\mathrm{H_2M}})$.

The differential equation

$$\frac{-\mathrm{d}(\mathrm{Cl_2})}{\mathrm{d}t} = \frac{k_2}{\sqrt{k_5}}(\overline{\mathrm{H_2M}})\sqrt{R}$$

follows from the mechanism considered above, except that reaction (5) replaces reaction (4) a chain breaking step; in the derivation the rate of reaction (5) was defined as

$$-\mathrm{d}(\mathrm{Cl})/\mathrm{d}t = k_5(\mathrm{Cl})^2$$

On integration of the differential equation for the rate of disappearance of chlorine the function

$$\frac{k_2}{\sqrt{k_5}} = \frac{\Delta(\mathrm{Cl_2})\sqrt{R}}{A\,(\overline{\mathrm{H_2M}})}$$

is obtained. The values of $k_2/\sqrt{k_5}$ which are calculated from the data are recorded in the last column of Table III. Comparison of experiments (1) and (2) shows, as is predicted by the mechanism, that the effect is independent of $(\mathrm{Cl_2})$ (the small difference observed in $k_2/\sqrt{k_5}$ is due to the fact that at the lower value of $(\mathrm{Cl_2})$, reaction (4) still partly operates as chain breaking step). In experiment (3), $(\overline{\mathrm{H_2M}})$ and $(\mathrm{Cl_2})$ were both decreased and the value of $k_2/\sqrt{k_5}$ checks with that in experiment (2). The effect of changing R and $(\overline{\mathrm{H_2M}})$ was studied with the inductor $\mathrm{Ti^{+++}}$. It is observed that $\Delta(\mathrm{Cl_2})$ varies inversely with R and varies directly with $(\overline{\mathrm{H_2M}})$, as is expected from the mechanism. It can be concluded that at high values of $(\mathrm{Cl_2})/(\overline{\mathrm{H_2M}})$ the observations are explained by the mechanism adopted.

The strongest evidence for the production of atomic chlorine by the reaction of one-electron reducing agents on $\mathrm{Cl_2}$[9] is the observation that $\mathrm{Ti^{+++}}$ gives nearly quantitatively the same effect as $\mathrm{Fe^{++}}$. The effect with $\mathrm{Ti^{+++}}$ is slightly greater because the reaction of this substance with chlorine, as shown by stirring experiments, is slower than for $\mathrm{Fe^{++}}$. The effect of stirring is fairly marked with $\mathrm{Fe^{++}}$ in this range of $(\mathrm{Cl_2})$, and it is possible that the maximum value was not reached at the highest stirring rate possible for the apparatus. There is no appreciable effect of stirring, for the same range of stirring rates,

---

chains are longer than expected. Such an effect is absent for $\mathrm{Fe^{++}}$, except possibly for the lowest values of $(\mathrm{Cl_2})$ in Table II where a continued increase in $\sqrt{k_2k_3/k_4}$ as $(\mathrm{Cl_2})$ decreases is observed.

[8] Similar effects have been observed in other cases for chain reactions in solution: Taube and Bray, THIS JOURNAL, **62**, 3372 (1940); Taube, *ibid.*, **64**, 2473 (1942).

[9] Analogous mechanisms have been proposed for the action of $\mathrm{Fe^{++}}$ (Hershey and Bray, THIS JOURNAL, **58**, 1760-1772 (1936); $\mathrm{Ti^{+++}}$ Yost and Zabaro, *ibid.*, **48**, 1181 (1926), and $\mathrm{Fe(CN)_6^{----}}$ (Wagner, *Z. physik. Chem.*, **113**, 261 (1924)) on $\mathrm{I_2}$.

TABLE III

The Kinetics of the Induced Reaction at High Values of $(Cl_2)/(H_2M)$; the Effect of Various Inductors: HCl = 1 *M*, $\mu = 1.0$

No.	Inductor	$A^a \times 10^5$	$R^a \times 10^4$	$(\overline{H_2M})$	$(Cl_2)_0 \times 10^2$	$(Cl_2)_t \times 10^2$	Chain length	$\frac{k_2}{\sqrt{k_5}}$
1	Fe^{++}	3.90	3.40	0.193	1.413	1.018	102	9.7
2	Fe^{++}	8.39	3.35	.198	3.463	2.453	120	11.2
3	Fe^{++}	8.26	3.25	.0973	1.627	1.117	62	11.4
4	Ti^{+++}	8.60	3.35	.198	3.192	2.076	130	12.0
5	Ti^{+++}	2.80	1.12	.200	3.070	2.450	222	11.5
6	Ti^{+++}	8 50	3.35	.110	3.116	2.484	74	12.5
7	Ti^{+++}	8.40	3.35	.053	3.088	2.785	36	12.5
8	Ti^{++}	9.76	3.80	.198	3.246	2.141	113	11.2
9	V^{+++}	8.32	3.32	.198	3.306	2.310	120	11.0
10	V^{+++}	2.54	3.54	.201	3.280	2.932	118	11.1
11	V^{++}	2.74	1.11	.200	3.242	2.647	217	11.4
12	V^{+++}	2.76	1.11	.200	3.295	2.806	177	9.3
13	V^{+++}	1.42	0.555	.201	3.394	3.131	186	6.9
14	V^{++}	8.15	3.33	.195	3.331	1.806	187	17.6
15[b]	V^{++}	2.76	1.11	.201	3.238	2.488	272	14.2
16	Mo^{+3} (r)	8.38	3.33	.201	3.206	2.868	40	3.7
17	Mo^{+3} (g)	8.47	3.33	.201	3.421	3.098	38	3.5

[a] For the solutions of Fe^{++}, Ti^{+++}, V^{++}, Mo^{+3}, *A* is expressed in moles per liter and *R* in moles per liter per minute; for V^{+++} and Ti^{++}, *A* is 2 × no. of moles per liter and *R* is 2 × no. of moles per liter per minute. Chain length = $\Delta(Cl_2)/A$. [b] In experiment (15), the solution was initially 10^{-4} *M* with respect to vanadate ion.

with Ti^{+++}, indicating that Ti^{+++} reacts slowly enough with chlorine so that it is uniformly distributed before it reacts. Furthermore, at low values of (Cl_2), the effect for Ti^{+++} increases relative to that of Fe^{++}, indicating that Ti^{+++} is not oxidized as rapidly as it is added, when (Cl_2) is low.

The results of experiments with other inductors are also contained in Table III. Experiments (8)–(11) show that Ti^{++}, V^{+++} and V^{++}, for the conditions obtaining in the experiments also produce the effect. If it is assumed that the ions Ti^{++} and V^{+++} are oxidized to the higher valence states (+4 and +5, respectively) by a sequence of two one-electron changes rather than directly by a two-electron change (which would produce $2Cl^-$ directly, without intermediate production of atomic chlorine) the results compare quantitatively with those for Fe^{++} and Ti^{+++}. Similarly, if V^{++} is oxidized by a two-electron change and a one-electron change (that is, each ion of V^{++} produces only one chlorine atom) the results for this reducing agent also agree.

However, $k_2/\sqrt{k_5}$, for V^{+++} decreases markedly as *R* decreases (Expts. (9), (10), (12) and (13)) for a range of *R* in which a similar comparison with Ti^{+++} still gives a constant value for $k_2/\sqrt{k_5}$; similarly, as *R* for the substance V^{++} increases, the value of $k_2/\sqrt{k_5}$ increases markedly (Expts. 11 and 14). These results can be understood if it is assumed that the direct reaction of V^{+++} and V^{++} with chlorine occurs by a two-electron change without production of atomic chlorine in this step, and that the product V^{+5} reacts very rapidly with V^{++} and V^{+++}.

$$V^{+5} + V^{+3} \longrightarrow 2V^{+4} \quad (8)$$
$$V^{+5} + V^{+2} \longrightarrow V^{+3} + V^{+4} \quad (9)$$
$$V^{+5} + \text{water} \longrightarrow V(OH)_4^+$$

The effect of reactions (8) and (9) is to produce V^{+4} and this substance is expected to react with chlorine by a one-electron process. At high values of *R*, the stationary concentration of V^{+5} will be high, reactions (8) and (9) for the consumption of V^{+++} and V^{++} will predominate, and the maximum induction effect will be observed. It should be stressed that the ions V^{+4} and V^{+5} are not identical with the stable ions VO^{++} and $V(OH)_4^+$, but probably have Cl^- rather than $O^=$ or OH^- attached to them. Thus VO^{++} is not rapidly oxidized by chlorine, and while $V(OH)_4^+$ (Expt. 15) does give an effect of the kind postulated for V^{+5}, a relatively high concentration is required.

Additional support for the processes discussed is furnished by the observation that while V^{++} and V^{+++} are oxidized to the +5 state under the conditions of the experiments, VO^{++} is the product if the reaction with chlorine is carried out with V^{++} (or V^{+++}) in excess (by adding Cl_2 to V^{++} or V^{+++} solution).

Another group of substances ($CuCl_2^-$, Cr^{++} and $Fe(CN)_6^{-4}$) was expected to, but did not, induce the reaction of chlorine with maleic acid. While the net reaction of these substances with chlorine yields a valence state higher by a one-electron change, the actual mechanism may correspond to an oxidation by a two-electron change (to a +3 state for Cu^{++}), followed by a rapid interaction of the +3 with the +1 state, as for example

$$Cu^+ + Cl_2 \longrightarrow CuCl^{++} + Cl^-$$
$$CuCl^{++} + Cu^+ = 2Cu^{++} + Cl^-$$

The value of $k_2\sqrt{k_5}$ for Mo^{+++} (Expts. (16) and (17)) is calculated on the assumption of a two electron + a one-electron change for the net oxidation to the +6 state; the effect observed is even less than corresponds to this assumption. It is possible that a one-electron change competes with a process analogous to that suggested for $CuCl_2^-$, for the oxidation of the complex +5 to +6 molybdenum. It should be observed that brown Mo^{+5} obtained by the reduction of Mo^{+6} in strong hydrochloric acid does not react rapidly with chlorine.

Sn^{++}, Hg_2^{++}, HNO_2, I^- proved to be without effect as inductors. Presumably the mechanism with these reducing agents corresponds to a two-electron change on reaction with Cl_2.

It may be worth while to stress that while positive quantitative effects observed for some of the reducing agents in the induced reaction under discussion point very strongly to a one-electron reduction of chlorine by some substance in the solution, negative effects may have a variety of explanations. The one suggested above—that the reducing agent acts by a two-electron change on chlorine—seems the most likely one. However, the possibility, with $CuCl_2^-$ for example, that the atomic chlorine reacts rapidly with the inductor is not ruled out. This interpretation seems less likely, since no evidence for a similar process with Fe^{++} was observed even at very low concentrations of Cl_2, where the lifetime of Fe^{++} would be relatively long.

On the basis of the mechanism presented, it is expected that a one-electron oxidizing agent (which would produce an organic free radical in the solution, or, if powerful enough, atomic chlorine) should also induce the chlorination of maleic acid. The result obtained with Ce^{+4} (Exp. 12 in Table II) shows that in fact quantitatively the same effect is obtained with this oxidizing agent as is observed with the reducing agent Fe^{++}. To control the rate of free radical production making it equal to the rate at which the inductor is added—the photo-chlorinated solution of maleic acid was used. Ce^{+4} reacts much more rapidly with dichlorosuccinic acid than it does with maleic acid or chloride ion; with 0.008 *M* dichlorosuccinic acid in the solution, Ce^{+4} is consumed as rapidly as it is added.

The mechanism proposed has been shown to be consistent with the observations on the kinetics of the reaction, and with the chemistry of the process. In the following, an attempt is made to associate other properties with the intermediates by a study of the effect of inhibitors. Table IV contains the report on these experiments. The concentration region in which reaction (5) (in the absence of inhibitors) is the main chain breaking step was selected for this study. Ferrous ion was used as the inductor.

TABLE IV

THE EFFECT OF INHIBITORS ON THE INDUCED REACTION

(HCl) = 1 *M* (except in Exp. 15), μ = 1.0, Temp. 25°. (I) means concentration of inhibitor; $R = 3.25 \times 10^{-4}$ for Expts. 1–4 and Exp. 15, and is 3.35×10^{-1} for the other experiments.

No.	I	(I) × 10³	$\overline{(H_2M)}$	$(Cl_2)_0 \times 10^2$	$A \times 10^5$	$\frac{\Delta(Cl_2)\sqrt{R}}{\overline{(H_2M)}A}$	$k_6/\sqrt{k_5}$
1	...	...	0.0973	1.627	8.26	11.4	..
2	Mn^{++}	0.0102	.0975	1.739	8.30	7.25	758
3	Mn^{++}	.0256	.0980	1.788	8.26	4.30	770
4	Mn^{++}	.0512	.0982	1.741	8.20	2.41	790
5	Mo^{+5}	2.31	.0990	1.604	8.61	3.13	13.4
6	VO^{++}	1.93	.0985	1.608	8.40	4.93	8.5
7	Cu^{++}	2.56	.0987	1.611	8.46	5.16	6.6
8	Co^{++}	5.12	.0985	1.634	8.46	5.93	2.5
9	Ce^{+++}	8.50	.0986	1.623	8.65	5.25	1.85
10	Pr^{+++}	12.0	.0976	1.773	9.04	8.95	0.79
11	Ni^{++}	14.6	.0978	1.745	8.65	9.60	.24
12	Cr^{+++}	19.5	.0978	1.748	8.45	9.80	.15
13	Fe^{+++}	19.5	.0976	1.668	8.54	9.85	.13
14	La^{+++}	25.5	.0973	1.820	8.61	11.3	..
15[a]	...	...	.0970	1.434	8.44	12.5	..

[a] In this experiment, $(H^+) = 0.280$; comparison of the figures in column 7 for experiments 1 and 15 shows that in the region of (H^+) employed, the reaction is almost independent of (H^+).

The following mechanism is suggested for the effect of the inhibitors

$$Mn^{++} + Cl \xrightarrow{k_6} Mn^{+++} + Cl^- \qquad (6)$$
$$Mn^{+++} + Fe^{++} = Mn^{++} + Fe^{+++} \qquad (7)$$

Reaction (7), a rapid follow reaction, accounts for the regeneration of the inhibitor. Regeneration of the inhibitor must take place for Mn^{++} since such small quantities are effective, and was proved for Ce^{+++} (no appreciable quantity of Ce^{+4} could be detected). It was assumed to be true for the other metal ion inhibitors. Whether the inhibitor is regenerated by process (7), by a reaction with an organic free radical, or by reaction with Cl_2^- (to give Cl_2) does not affect the relative values calculated for k_6.

The values of $k_6/\sqrt{k_5}$ were calculated from the expression[10]

$$\Delta(\mathrm{Cl_2}) = \frac{k_2\,(\overline{\mathrm{H_2M}})}{\sqrt{k_5}}\left[\sqrt{\left(\frac{k_6\,(\mathrm{I})}{\sqrt{k_5}}\right)^2 + R} - \frac{k_6\,(\mathrm{I})}{\sqrt{k_5}}\right]t$$

which is based on a mechanism in which reactions (5) and (6) compete as chain breaking steps.

Experiments (2), (3) and (4) show that the reaction of Mn^{++} with the intermediate is indeed first order with (Mn^{++}) since the value of $k_6/\sqrt{k_5}$ is constant as (Mn^{++}) varies.

Evidence that the intermediate which reacts with the inhibitor is a powerful one-electron oxidizing agent is furnished by the observation that Mn^{++}, VO^{++}, Mo^{+5} (brown), Co^{++}, Ce^{+++} and Pr^{+++} are all inhibitors. These are known to have valence states higher by a one electron change. A remarkable result is that the Cu^{++} is also an efficient inhibitor; the suggestion is again[11] made that chlorine atoms can oxidize Cu^{++} to the +3 state. The results in Table IV show that the ions Ni^{++}, Fe^{+++}, Cr^{+++}, which are known to have higher oxidation states, can be oxidized, though not readily, to intermediate states by atomic chlorine. Experiment (14) shows that La^{+++} does not affect the reaction; it can be added that NO_3^- and $SO_4^=$ in about 0.01 *M* solution, are also without effect.

The relative values of k_6 presented in Table IV can be useful in identifying atomic chlorine as the intermediate in other reactions in solutions of high Cl^- content. Evidence for the presence of an organic free radical in the solutions is the observation that oxygen inhibits the reaction. For example, without removal of oxygen, the indirect effect in Exp. (3) Table II would be almost zero, and would appear only if larger quantities of Fe^{++} were added. It appears that an induced oxidation supplants the chlorination reaction[12] when the concentration of oxygen is appreciable, and the chlorination proceeds only after the oxygen is almost completely consumed.

Qualitative experiments on the photochemical chlorination of maleic acid in aqueous solution have shown that this reaction also is a chain reaction, and that it is strongly inhibited by oxygen and manganous ion. These observations suggest that the mechanism is the same for the induced and photochemical reactions and provide additional support for the interpretation of the results. Experiments on a quantitative comparison of the induced and photochemical reaction are now in progress.

Summary

Results on the induced chlorination of maleic acid have been presented and discussed.

One-electron reducing agents which react with Cl_2, and Ce^{+4}, were shown to be equally effective as inductors.

One-electron reducing agents which do not react rapidly with Cl_2, were shown to be effective as inhibitors of the induced reaction. O_2 is also an efficient inhibitor.

These results, and the kinetics of the process, are explained by a chain mechanism involving atomic chlorine and an organic free radical.

The relative rates of reaction of atomic chlorine in 1 *M* Cl^- at 25° with a variety of inhibitors and with maleic acid have been tabulated.

ITHACA, N. Y. RECEIVED MAY 27, 1943

---

[10] $k_2/\sqrt{k_5}$ is known from the blank experiment, $\Delta(Cl_2)$ and t are measured, (I) = concentration of the inhibitor, ($\overline{H_2M}$) and R are known so $k_6/\sqrt{k_5}$ remains as the only unknown.

[11] Reference 1, p. 3366.

[12] Effects of this kind have been observed in many photochemical halogenation reactions: ref. 2, pp. 329–340.