uses a hydrogen arc as a source of ultraviolet radiation and a photocell-amplifier combination as a detector. The spectral region covered was from 2230 to 4000Å.

Solutions of known concentration were made by dissolving weighed quantities of solute in ethyl ether in a volumetric flask. At least two different concentrations of solute were used in most cases since a wide range in molecular extinction coefficient was encountered. The solution was poured into one of two matched silica absorption cells and the second cell was filled with solvent. Both cells were then inserted into the spectrophotometer and the intensity of light passing through each of them was recorded. The temperature of the solutions was maintained between 22 and 25°.

Extinction coefficients were calculated from the familiar equation

$$\epsilon = \frac{1}{cd} \log_{10} (I_0/I)$$

where I_0 is the intensity of the light passing through the solvent, I, the intensity of the light passing through the solution, c, the concentration of solute, in moles per liter, and d the thickness of the cell, in centimeters.

The compounds examined were prepared in the following ways.

Cholesteryl Methyl Ether.—The normal ether was prepared by the reaction of cholesteryl *p*-toluenesulfonate with methanol. Repeated crystallization from acetone gave platelets melting at 84–84.5°.

***i*-Cholesteryl Methyl Ether.**—The isomeric methyl ether was prepared from cholesteryl *p*-toluenesulfonate by the method of Stoll.[8] The crude ether was crystallized many times from acetone. Long, thin rods were obtained and melted at 79–79.8°.

***i*-Cholestenone.**—3(α)-Chlorocholestanone-6 was converted into *i*-cholestenone by the method of Windaus and Dalmer.[9] After several crystallizations from methanol, the ketone was sublimed at 75–80° at 10^{-4} mm. Crystallization of the sublimate from methanol gave a product melting at 93–96°. The above compounds were prepared by Dr. Edwin W. Meyer.

3-Cholestanone.—The method used for the preparation of 3-cholestanone was that described by Bruce.[10] The compound was crystallized from dilute ethanol until spectrographically pure. Dr. Irving Allan Kaye prepared this ketone.

Δ^6-*i*-Cholestadiene.—This material melted at 73–73.5° and gave a specific rotation of −60.9°. Its method of preparation and chemical characterization will be described in a publication[11] that will appear shortly.

***d*-5-Carone.**—Dihydrocarvone, b. p. 116–118° (17 mm.), was prepared in 62% yield from carvone by the method of Wallach.[12] It was converted to dihydrocarvone hydrochloride by passing in dry hydrogen chloride until 120% of the theoretical amount had been absorbed. This crude product was converted directly to *d*-5-carone by the method of Richter, Wolff, and Presting.[13] The crude *d*-5-carone was dissolved in 5 to 6 volumes of Skellysolve F (petroleum ether, b. p. 30–60°) and the resulting solution was washed with an excess of neutral potassium permanganate solution (20 g. of potassium permanganate and 25 g. of sodium bicarbonate per liter of solution), heated on the steam-bath to remove the Skellysolve F, and distilled under reduced pressure. The yield was 67%, b. p. 115–116° (15 mm.), $d^{26}{}_4$ 0.933, $[\alpha]^{25}\text{D}$ +155.6° ($\alpha^{25}\text{D}$ 143.3°, *l*, 1 dm.). The *d*-5-carone was prepared and purified by Dr. R. I. Jackson.

α-Pinene.—A commercial product was distilled and a fraction which boiled at 158.5–159.0° was used.

β-Pinene.—A very pure commercial sample was used without further treatment; b. p. 165.8°.

Camphene.—The product examined was obtained from *i*-borneol by dehydration. It had a melting point of 50°.

Bicyclo-[2,2,1]-2-heptene.—This compound was obtained by treating cyclopentadiene and ethylene by the method described by Joshel and Butz.[14] A sample was redistilled and then recrystallized twice from an ethyl alcohol–water mixture. The product melted at 53°.

The samples of α-pinene, β-pinene, camphene and bicyclo-[2,2,1]-2-heptene were supplied by Dr. H. Pines.

Summary

The absorption spectra of a number of compounds containing a cyclopropane ring adjacent to an olefinic or carbonyl group have been examined and have been interpreted in terms of resonance due to hyperconjugation.

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[8] W. Stoll, *Z. physiol. Chem.*, **207**, 147 (1932).

[9] A. Windaus and O. Dalmer, *Ber.*, **52**, 168 (1919).

[10] W. F. Bruce, "Org. Syntheses," Coll. Vol. II, p. 139.

[11] Unpublished results of B. Riegel, G. P. Hager and B. L. Zenitz.

[12] O. Wallach, *Ann.*, **279**, 377 (1894).

[13] F. Richter, W. Wolff and W. Presting, *Ber.*, **64**, 877 (1931).

[14] L. M. Joshel and L. W. Butz, THIS JOURNAL, **63**, 3350 (1941).

EVANSTON, ILLINOIS RECEIVED JULY 8, 1943

[COMMUNICATION NO. 951 FROM THE KODAK RESEARCH LABORATORIES]

Ascorbic and Iso-ascorbic Acids as Photographic Developing Agents

BY T. H. JAMES

Ascorbic and iso-ascorbic acids represent a type of developing agent chemically quite distinct from the conventional aromatic agents. The developer activity of ascorbic acid was first reported by Maurer and Zapf[1] in 1934. Shortly afterwards, Bills[2] published formulas in which ascorbic acid was the active developing agent, and Rzymkowski[3] and Pavolini[4] published similar formulas for iso-ascorbic acid. Reaction mechanism studies have not been reported.

The present paper is concerned chiefly with establishing the general kinetics of development by ascorbic and iso-ascorbic acids, preliminary to using these substances in an investigation of the electric charge effect[5] in development. They show certain definite advantages over the aromatic agents usually employed for this purpose. The most important advantage is that the oxidation products of the ascorbic acids do not

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[1] K. Maurer and G. Zapf, *Ber.*, **67**, 1239 (1934); *Phot. Ind.*, **33**, 90 (1935).

[2] C. E. Bills, *Science*, **81**, 257 (1935).

[3] J. Rzymkowski, *Phot. Ind.*, **33**, 91 (1935).

[4] T. Pavolini, *Il Corr. Fot.*, **32**, 33 (1935).

[5] T. H. James, *J. Phys. Chem.*, **43**, 701 (1939).

interfere with the development process. The kinetic conditions are thus considerably simplified.

Materials and Methods

Ascorbic Acids.—Eastman Kodak Company *l*-ascorbic acid and *d*-iso-ascorbic acid were used.

Alkali and Salts.—General Chemical Company reagent grade potassium hydroxide and salts were used.

Water was redistilled in an all-Pyrex glass apparatus.

All development operations were carried out at 20 ± 0.05° under an atmosphere of oxygen-free nitrogen, using the general procedure previously described.[5] A series of development tests made on solutions which had been kept in the development apparatus for times varying from ten minutes to twenty-four hours gave satisfactorily constant results.

The photographic material was a normal motion picture positive (silver bromide) emulsion. Strips of film were given standard exposures in the Eastman Type IIb sensitometer. The step corresponding toan exposure of $\log E = 1.15$ (where E is in meter-candle-seconds) was employed in general for rate determinations. This exposure step was consistently on the "straight-line" portion of the exposure curve.[6] Rates are given in terms of R, the slope of the density–time curve of development at $D = 0.80$; and $1/t$, where t is the time required to obtain a density of 0.20.

Comparison of Ascorbic and Iso-ascorbic Acids.—At *p*H 10.3, the R values for iso-ascorbic acid in several experiments varied from 1.30 to 1.37 times those of ascorbic acid, with an average of 1.32. The ratio of $1/t$ values varied from 1.34 to 1.50, with an average of 1.45. In 0.04 M excess potassium hydroxide solution, the R values for iso-ascorbic acid varied from 1.0 to 1.09 times those of ascorbic acid, with an average of 1.03. The ratio of $1/t$ values varied from 1.1 to 1.2, with an average of 1.14. Thus, the iso-ascorbic acid develops appreciably faster than the ascorbic at *p*H 10.3, but only slightly faster in the caustic solution. No difference was noted in the rate of fog formation by the two substances.

Experiments carried out under varying conditions showed no significant difference in the general developing properties of the two acids. More complete data were obtained for the iso-ascorbic acid, and only these results will be reported subsequently.

Effect of Bromide Ion.—The addition of potassium bromide to the developing solution decreased the rate of image development, but had a much greater effect in depressing the rate of fog formation. Data are listed in Table I. The rate of fog formation is indicated by the last column. In the subsequent work, sufficient bromide was employed to suppress fog formation to a small, and generally negligible, quantity.

TABLE I

EFFECT OF BROMIDE ON DEVELOPMENT BY ISO-ASCORBIC ACID

*p*H	KBr concn.	R	$1/t$	Time for fog $D = 0.10$
10.33	.....	0.030	....	36
10.33	0.00067	.025	0.0125	110
10.33	.00667	.018	.0085	192
KOH				
0.04 M	.00067	.07	.048	22
.04 M	.0020	.065	.050	28
.04 M	.0067	.05	.040	>42

Effect of Concentration and *p*H.—The variation in rate with concentration of iso-ascorbic acid is given in Table II. The salt environment was maintained essentially constant. The solutions of *p*H 10.34–10.38 contained 0.167 M potassium carbonate and sufficient bicarbonate or hydroxide to adjust the *p*H. The caustic solutions contained 0.333 M potassium nitrate. The total potassium-ion concentration was approximately 0.35 in the carbonate solution and 0.39 in the caustic solution.

The variation in rate with *p*H is given in Table III. A carbonate buffer was used in all experiments except the one at *p*H 7.96, where a phosphate buffer was employed.

TABLE II

VARIATION OF DEVELOPMENT RATE WITH ISO-ASCORBIC ACID CONCENTRATION

Iso-ascorbic concn.	*p*H	R	$1/t$	KBr concn.
0.0025	10.34	0.038	0.021	0.00067
.0050	10.34	.064	.041	.00067
.0100	10.36	.112	.083	.00067
.0150	10.38	.170	.125	.00067
.0025	0.04 M KOH	.062	.050	.00667
.0050	.04 M KOH	.126	.105	.00667
.0100	.04 M KOH	.235	.23	.00667

TABLE III

EFFECT OF *p*H UPON DEVELOPMENT RATE

Iso-ascorbic acid, 0.005 M; KBr, 0.00067 M

*p*H	R	$1/t$	$\%$ A$^-$
7.96	...	0.002	...
10.08	0.042	.025	3.5
10.25	.051	.036	5.1
10.35	.065	.041	6.3
10.55	.083	.056	9.6

Effect of Oxidation Products and Copper.—The oxidation products of iso-ascorbic acid were without any effect upon the rate of development, so far as could be detected. The addition of partially oxidized iso-ascorbic acid and the admission of small amounts of oxygen were without effect other than a minor one due to some alteration in the concentration of the developing agent. The addition of copper salts, which markedly catalyze the oxygen oxidation of ascorbic acid (at least in acid and neutral solutions), produced, if anything, a slight *decrease* in the development rate.

Temperature Coefficient.—At *p*H 10.15, the 10° temperature coefficient over the range 8–20° was about 2.55 for R rates, and 1.85 for $1/t$ rates. In the caustic solution, the coefficient

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[6] Details on the standard exposure treatment and general photographic terminology are given in "The Theory of the Photographic Process," by C. E. K. Mees, the Macmillan Co., New York, N. Y., 1942.

was 1.90 for R, and 1.75 for $1/t$ over the same temperature range. In each case, the solution contained 0.333 M potassium nitrate and approximately 0.04 N potassium carbonate or potassium hydroxide.

Neutral Salt Effect.—A careful control of the salt environment proved to be essential to the kinetic investigation. The rate of development is markedly dependent upon the concentration of neutral salts. The magnitude of this effect is indicated by the results given in Tables IV and V.

The increase in the development rate was accompanied by some increase in the photographic emulsion speed. The nature of this increase, together with a more complete investigation of the salt effect, will be considered in a subsequent paper. Both have a bearing upon the general question of the effect of the electric charge upon the over-all kinetics of development.

TABLE IV

NEUTRAL SALT EFFECT

K_2CO_3, 0.033 M; iso-ascorbic acid, 0.005 M

Salt	Concn.	pH	R	$1/t$	KBr
..	..	10.33	0.0246	0.0125	0.00067
KNO_3	0.167	10.25	.052	.0345	
	.333	10.18	.073	.045	
	.667	10.12	.085	.067	
NaAc	.167	10.26	.047	.027	
Na_2SO_4	.0667	10.26	.0346	.023	
	.1333	10.22	.043	.029	
	.333	10.13	.051	.0345	
$Na_2C_2O_4$	.167	10.22	.046	.033	
$K_2C_2O_4$	.167	10.18	.062	.043	
K_2SO_4	.167	10.19	.063	.043	
K_2CO_3 $KHCO_3$	.133 .0067	10.33	.065	.040	
..	..	10.33	.0182	.0085	.00667
KNO_3	.1333	10.27	.036	.020	
	.333	10.18	.064	.031	
	.667	10.12	.072	.043	
	1.333	10.13	.090	.054	

TABLE V

NEUTRAL SALT EFFECT

Iso-ascorbic acid, 0.005 M; excess KOH, 0.04 M; KBr, 0.00667 M.

Salt	Concn.	R	$1/t$
..	....	0.050	0.040
KNO_3	0.1333	.086	.071
	.333	.166	.105
	.667	.186	.156
	1.333	.235	.217

Discussion

In the presence of a suitable amount of bromide ion, ascorbic and iso-ascorbic acids yield good image development with only slight fog formation. The acids show no unusual properties as developing agents. In general, they resemble hydroquinone. The one important point of difference is the lack of any measurable effect of the oxidation products upon the course of development.

At pH 8.0, where the ascorbic acid exists almost entirely as the univalent ion, development is feeble. In the more alkaline solutions, the bivalent ion is responsible for almost all of the developing activity. This is shown by the data in Table III. A plot of log R against log $A^=$, where $A^=$ is the percentage of bivalent ion calculated on the basis of a dissociation constant of 3×10^{-12}, yields a nearly straight line of slope 0.75. A similar plot of log R against log C for varying concentrations of the acid at pH 10.35 gives a straight line of slope 0.78. Thus, the rate is determined by the concentration of the bivalent ion. The fact that the dependence is less than linear suggests adsorption of the ion prior to reaction with the silver halide. Similar results were obtained previously with hydroquinone.[7]

The $1/t$ rates are nearly proportional to the ascorbic acid concentration, but show a somewhat smaller dependence upon the $A^=$ values for varying pH. It is possible that the rate of diffusion through the double-layer region of the silver bromide grain is already of importance in determining the measured rate during this initial stage of development. The lower temperature coefficient of the $1/t$ values in comparison with the R values supports this possibility.

Diffusion rates become important in the caustic solution. The rates of development are only about one-fourth as great as those expected on the basis of the rates at pH 10.35. Comparisons must be made, of course, at equal salt concentrations, but the necessary data are available in Tables IV and V. Moreover, R is nearly proportional to the ascorbic acid concentration in the caustic solution. This is in contrast to the situation in the lower pH region, and is not to be expected if reaction rates are the determining factor. The decrease in temperature dependence observed in passing from pH 10.3 to a caustic solution is in line with the preceding interpretation, although the temperature dependence in development is complex and theoretical interpretations based upon it at the present time are of doubtful value. Finally the fact that ascorbic and iso-ascorbic acids show nearly equal rates in the caustic solution, in contrast to the observations at lower pH, favors diffusion as an important rate-determining factor. An alternative interpretation, that the second dissociation constant of iso-ascorbic acid is larger than that of ascorbic acid, is not supported by published data.[8]

The data on the effect of neutral salts show how important this factor can be in determining the rate of development by ascorbic acid (and other doubly-charged negative ions). Increases in rate up to five- and sixfold were produced solely by added neutral salt. Trace catalysis

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(7) T. H. James, *J. Phys. Chem.*, **44**, 42 (1940).

(8) *Cf.* G.-E. Carpéni, *J. chim. phys.*, **35**, 193 (1938).

produced by impurities in the salts is not involved in this effect. Samples of potassium nitrate obtained from three very different sources gave identical salt effects. Two samples of sodium sulfate, one impure, the other highly purified, gave results identical within the limit of experimental error.

The salt effect is caused by a depression of the double-layer zeta-potential of the silver bromide.[5] This permits a greater penetration of the bivalent ascorbic acid ions through the double-layer region to the surface of the grain, where the development reaction takes place.

Summary

The course of photographic development by *l*-ascorbic and *d*-iso-ascorbic acids is not affected by the oxidation products. The iso-ascorbic acid reacts at a somewhat greater rate than the ascorbic acid.

At *p*H 10 or above, the active developer consists almost entirely of the bivalent ion. This ion is adsorbed prior to reaction with the silver bromide. In caustic solution, diffusion rates become important in determining the measured development rate.

The rate of development is markedly dependent upon the nature and concentration of the salts present. The rate increases with increasing salt concentration.

ROCHESTER, N. Y. RECEIVED OCTOBER 4, 1943

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Molecular Structures of Dimethyl Silicon Dichloride, Methyl Silicon Trichloride and Trifluoro Silicon Chloride[1]

BY R. L. LIVINGSTON AND L. O. BROCKWAY

Previous study of the mutual interaction of groups attached to a central silicon atom left several unanswered questions. For example, the substitution of one or two hydrogen atoms into silicon tetrachloride has no detectable effect on the length of the Si–Cl bond,[2] but in silicon tetramethyl the replacement of one methyl group by a silicon atom (as in the molecule $(CH_3)_3SiSi(CH_3)_3$[3] apparently shortens the Si–C bonds by one and one-half per cent. An extension of the study of the interaction between atoms attached to silicon was made possible by the availability of samples of methyl silicon trichloride and dimethyl silicon dichloride. Another question of interest in silicon compounds is the interaction of attached fluorine atoms. In the organic fluorides the presence of two or more fluorine atoms on the same carbon shortens the C–F bond by 0.06Å. below the length observed in the monofluorides,[4] while the effect of the CF_3 group in CF_3Cl[5] on the attachment of the chlorine atom is equally marked in comparison with the bond lengths in carbon tetrachloride. This effect in the analogous silicon compound has now been studied. The methyl silicon chlorides were supplied by W. F. Gilliam of the General Electric Research Laboratories, and the trifluoro silicon chloride was supplied by H. S. Booth of Western Reserve University.

Electron diffraction photographs of the vapors were prepared in the usual way using an electron wave length of 0.0592Å. and a camera distance of 10.29 cm. The specimens were handled on a vacuum line and transferred to the camera without admitting air in order to reduce possible hydrolysis by water vapor. For each compound the s_0 values $(4\pi(\sin \Theta/2)/\lambda)$ calculated from the visually measured ring diameters are tabulated together with the coefficients used in the radial distribution function, $D(r) = \Sigma C_k \sin s_k r/s_k r$. The radial distribution curves (Fig. 1) indicate by their stronger maxima the values of interatomic distances associated with the more important scattering terms.

Methyl Silicon Trichloride.—Photographs of methyl silicon trichloride taken with the sample held near 25° show nine rings in the range out to $s = 23$. The measurements on the last eight are listed in Table I. The fourth maximum appears as a satellite to the stronger third maximum; its measured position is accordingly unreliable. The sixth maximum is broad with a faint inner shelf which was not measured. The eighth minimum is broad without a well-defined lightest point.

Scattering curves were calculated for four models in each of which the Si–C bond was assumed to lie on an axis of trigonal symmetry, the methyl group was assumed to have the regular tetrahedral bond angles with C–H = 1.09 Å., and the Si–Cl distance was set at 2.00 Å. to fix the scale of the models. In three models the Si–C/Si–Cl ratio was 0.970 with the $\angle$ClSiCl equal to 113° (model A), to $109^1/_2$° (model B) and to 106° (model D). In model C the bond distance ratio was 0.935 with a chlorine bond

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[1] This paper represents part of a dissertation submitted to the Horace H. Rackham School of Graduate Studies by R. L. Livingston in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] L. O. Brockway and I. E. Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

[3] L. O. Brockway and N. R. Davidson, THIS JOURNAL, **63**, 3287 (1941).

[4] L. O. Brockway, *J. Phys. Chem.*, **41**, 747 (1937).

[5] L. O. Brockway and John H. Secrist, in publication.