

other hand gives the complexes $(\text{Fe}_2\text{C}_2\text{O}_4)^{---}$ (inactive) and $(\text{Fe}_3\text{C}_2\text{O}_4)^{+++}$ (active). With cobalt, both complexes, the green as well as the pink, contain divalent Co, in the ratio of $\text{C}_2\text{O}_4^{---}/\text{Co}^{++} = 1$, but they differ in their internal structure. The green cobalto-citrate complex proved to be the most sensitive catalyst of all the complex citrates studied by us for the decomposition of hydrogen peroxide.

The study of the structure of the citrate complexes compared with that of tartrate complexes will be the object of a special article. Di-sodium tartrate too yields with hydrogen peroxide a green complex which catalyzes the decomposition of the peroxide, but the tartrate is simultaneously attacked by the peroxide, gives a precipitate and is therefore unfit for study. The parallel study of Co^{++} and Fe^{+++} -citrate and -tartrate complexes gives a possibility for a deeper insight into the structure of these substances. It might be supposed that in the case of citrate (with only one oxy-group) complexes the hydrogen of the oxy-group is replaced by a metal valence and a stable compound is thus produced, while in the active form the metal may be found in another way through a secondary valence to the oxy-anion.

By comparison with cobalto-ammonia complexes which also catalyze the decomposition of hydrogen peroxide,² it seems probable that the structural difference between pink and green

cobalto-citrate complexes is that in the case of the green complex the cobalt atom is linked to the citrate by a secondary valence, while the linking is much stronger in the case of the pink complex.

Summary

A mixture of Co^{++} and $\text{C}_2\text{O}_4^{---}$ ions (pink complex) with hydrogen peroxide in the ratio $1\text{Co}^{++}/1\text{C}_2\text{O}_4^{---}/1\text{H}_2\text{O}_2$ immediately leads to a pink peroxidized compound (without change of color), which decomposes gradually with liberation of all the disposable oxygen into a green divalent cobalt citrate complex. This green complex can also be obtained by peroxidizing the pink cobalto-citrate complex with lead or manganese dioxide instead of hydrogen peroxide. The green cobalto-citrate complex thus obtained acts as an extremely active catalyst (the most active of all the complex citrates) for the decomposition of hydrogen peroxide, but it cannot decompose lead or manganese dioxides. During all these operations the citrates are not attacked at all while corresponding reactions with tartrates lead to attack of the tartrate ion.

The properties of the complexes were studied by gasometric, photometric and conductometric methods.

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⁽⁹⁾ Reported to have been dispatched from Jerusalem on February 25, 1941, but suffered various vicissitudes.

NOTES

The Catalytic Effect of Electrolytes on Solvolytic Reactions

By L. F. AUDRIETH, L. D. SCOTT AND O. F. HILL

In a series of publications from this Laboratory¹ it has been demonstrated experimentally that ammonolytic and aminolytic reactions, involving the action of ammonia and amines upon esters, are catalyzed, respectively, by ammonium and amine salts presumably acting as acids in these solvents. In order to characterize still further the catalytic effects of various classes of substances upon solvolytic reactions in general, the influence of electrolytes (salts) upon the reactions (a) be-

tween *n*-butylamine and ethyl phenylacetate and (b) between liquid ammonia and ethyl benzoate were subjected to study. The experimental results presented below show (a) that additions of relatively small quantities of various neutral salts speed up effectively the conversion of the esters into the corresponding solvolytic products; (b) that the catalytic effect of equimolar concentrations of these salts is not nearly as marked as for the corresponding "onium" salts; and (c) that the findings heretofore considered as evidences for acid catalysis in basic solvents by the solvated proton may be but special cases of what might more properly be regarded as examples of electrolyte catalysis.

⁽¹⁾ See Glasoe, Scott and Audrieth, *THIS JOURNAL*, **63**, 2965 (1941), for earlier articles.

Experimental

The experimental procedures employed in studying these reactions have already been described in previous publications.^{2,3} The data presented in Table I constitute a summary of the results obtained using various electrolytes, and electrolytes plus definite additions of water, in *n*-butylamine. The essential data for the reaction between liquid ammonia and ethyl benzoate are given in Table II. For purposes of comparison some data are also included in both tables of results previously reported on the catalytic effect of the corresponding "onium" salts. In both cases the observed catalytic effects are emphasized in the last column in which are given the experimentally determined half time values (in hours) for each series of runs.

TABLE I
AMINOLYSIS OF ETHYL PHENYLACETATE IN *n*-BUTYL-AMINE AT 25°

a = concn. of amine in moles per liter; *b* = concn. of ester in moles per liter.

Catalyst	Concn. of catalyst in moles per liter	<i>a</i>	<i>b</i>	<i>K</i> × 10 ³	<i>t</i> ^{1/2} (exp.)
None ^a	...	5.45	2.80	0.87	158
NaClO ₄	0.1	5.38	2.80	1.55	92
C ₄ H ₉ NH ₂ ·HClO ₄ ^a	.1	5.40	2.80	2.09	70
NaI	.1	5.37	2.81	2.06	73
NaI	.2	5.30	2.81	2.50	59
C ₄ H ₉ NH ₂ ·HI ^a	.1	5.34	2.80	2.57	57
NaSCN	.1	5.37	2.81	2.07	73
NaSCN	.2	5.42	2.77	2.39	63
C ₄ H ₉ NH ₂ ·HSCN ^a	.1	5.36	2.80	2.81	53
NaSCN } H ₂ O }	.2 } 2.0 }	4.91	2.81	4.7	36
NaI } H ₂ O }	0.2 } 2.0 }	5.11	2.81	5.7	26

^a Taken from data summarized in ref. 3.

TABLE II
AMMONOLYSIS OF ETHYL BENZOATE IN LIQUID AMMONIA AT 0°

Moles C₆H₅COOC₂H₅ = 0.035; moles NH₃ = 0.082 ± 0.3; moles catalyst = 0.00935.

Catalyst	<i>K</i> × 10 ⁴	<i>t</i> ^{1/2} (exp.)
None	0.47	ca. 15000
NH ₄ Cl ^a	7.86	882
NaCl	2.52	2760
NaNO ₃	1.28	5420

^a Taken from data summarized in ref. 2.

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- (2) Fellingner and Audrieth, *THIS JOURNAL*, **60**, 579 (1938).
(3) Glasoe, Kleinberg and Audrieth, *ibid.*, **61**, 2387 (1939).

Attempt to Detect Free Hydroxyl as an Intermediate in Photochemical Reactions

By W. J. BLAEDEL,¹ R. A. OGG, JR., AND P. A. LEIGHTON

Free hydroxyl has been proposed as an intermediate in several photochemical processes.^{2,3} The mechanisms of all the following processes might involve this substance (at 2537 Å.)

- (1) CH₃I + O₂ + *hν*
- (2) H₂O₂ + *hν*
- (3) H₂O₂ + Hg + *hν*
- (4) H₂O + Hg + *hν*
- (5) H₂ + O₂ + Hg + *hν*
- (6) CH₃OH + Hg + *hν*

In any of these processes, if the reactions by which hydroxyl disappears have low rates compared to those by which it is formed, it is conceivable that steady-state concentrations might be attained which are sufficient to be detectable by the absorption spectrum. The purpose of the following work was to detect such absorption if possible.

Experimental.—The photochemical reaction vessel was a cylindrical quartz tube, 120 cm. long, and 3.5 cm. in diameter, with plane quartz end windows. Irradiation was effected by placing two low pressure mercury arcs, each 120 cm. long and 0.7 cm. in diameter, parallel to and on opposite sides of this tube. A cylindrical aluminum reflector, open at the ends, enclosed the arcs and quartz tube.

Light from a water discharge giving the 3064 Å. hydroxyl band in emission was passed lengthwise through the reaction cell and into the slit of a 21-ft. concave grating spectrograph. The intensity of the discharge in the region containing the Q₁ 1^{1/2} and Q₁ 2^{1/2} lines was measured in the focal plane of the spectrograph with a sensitive photocell-amplifier system. This region shows the highest absorption at room temperature. The absorption noted in this region when the low pressure arcs were turned on was taken as a measure of the steady-state hydroxyl concentration produced.

The limit of detection of hydroxyl was determined by a method similar to that of Oldenberg and Rieke,⁴ by measuring the absorption of water vapor dissociated at a high temperature. Here, the quartz cell was replaced by a cylindrical furnace with quartz end windows. Oxygen and water vapor at known pressures were passed through this furnace at about 1400° Å. The temperature distribution was measured along the furnace axis with a Pt/Pt-Rh thermocouple. Zeise's data⁵ on the dissociation constants of water at various temperatures enabled a calculation of the hydroxyl distribution along the furnace axis at the high temperature. From the rotational term levels of the hydroxyl molecule,⁴ the absorption of this same distribution at room temperature was calculated. This, with the

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- (2) Urey, Dawsey and Rice, *THIS JOURNAL*, **51**, 1371 (1929).
- (3) Bates and Spence, *ibid.*, **53**, 1689 (1931).
- (4) Oldenberg and Rieke, *J. Chem. Phys.*, **6**, 439 (1938).
- (5) Zeise, *Z. Elektrochem.*, **43**, 704 (1937).