methoxide for one-half to one hour. The steroid was isolated *via* a digitonin precipitation and obtained free in the usual manner by pyridine cleavage of the digitonide. From the non-digitonin precipitable fraction the α-naphthylurethan of methyl alcohol was isolated and recrystallized twice from ligroin; m.p. 121–122°, mixed melting point with authentic urethan, 122–124°.

A model DU Beckman spectrophotometer was used in the determination of the ultraviolet spectra. The infrared spectra of the steroid derivatives, mulled in nujol, were recorded with a Perkin–Elmer model 21 spectrometer equipped with a sodium chloride prism. We are grateful to Roger A. Pickering for obtaining the infrared data.

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Evidence for Carbonium Ion Formation from Crystal Violet in Concentrated Sulfuric Acid

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RECEIVED MARCH 28, 1955

It has been well established that triphenylcarbinol and many substituted triphenylcarbinols ionize in sulfuric acid to give stable carbonium ions, according to the equation

$$(C_6H_5)_3COH + 2H_2SO_4 \longrightarrow (C_6H_5)_3C^+ + 2HSO_4^- + H_3O^+$$

The solutions are intensely colored, give *i*-factors of 4.0 by cryoscopic measurements, and undergo various reactions typical of carbonium ions.

When the carbinol contains three dimethylamino groups, as in crystal violet, the ionization in sulfuric acid would be expected to be accompanied by protonation of one or more of the dimethylamino groups. Newman and Deno[1] obtained an *i*-factor of 6.0 for crystal violet in 100% sulfuric acid; the solution was orange-brown in color. The ionization was assumed to be

$$((CH_3)_2NC_6H_4)_3COH + 4H_2SO_4 \longrightarrow ((CH_3)_2\overset{+}{N}HC_6H_4)_2\overset{+}{C}C_6H_4N(CH_3)_2 + H_3O^+ + 4HSO_4^- \ (i = 6.0)$$

An *i*-factor of 6.02 was obtained for the analogous tri-*p*-aminophenylcarbinol, with the same type of ionization assumed.

Branch and Walba[2] have reported measurement of the spectrum of crystal violet in concentrated sulfuric acid[3] and reported that no bands were present from 275–700 mμ. The explanation offered is that all three dimethylamino groups are protonated, thereby increasing the positive charge on the molecule to the extent that any carbonium ion, if formed, reacts with a bisulfate ion to give a benzenoidal ion

$$((CH_3)_2NC_6H_4)_3COH + 5H_2SO_4 \longrightarrow ((CH_3)_2\overset{+}{N}HC_6H_4)_3CHSO_4 + 4HSO_4^- + H_3O^+$$

This benzenoidal ion should possess no color. It should be noted that the formation of the benzenoidal ion in sulfuric acid also leads to an *i*-factor of 6.0, so that cryoscopic measurements *alone* cannot indicate whether a carbonium or benzenoidal ion is present.

The different interpretations of the behavior of crystal violet in sulfuric acid solution as presented by Newman and Deno on the one hand and Branch and Warba on the other appear to stem from conflicting observations. The orange-brown color observed by the former experimenters is hardly compatible with the complete lack of bands throughout the range of 275–700 mμ as reported by the latter workers. Newman and Deno synthesized their tri-*p*-dimethylaminophenylcarbinol by previously described methods,[4] while Branch and Warba purified commercial crystal violet by recrystallization. No melting points or analytical data are recorded in either case. It is possible that the commercial sample may have been the triphenylmethane derivative which is also known as crystal violet. In view of these possibilities it seemed advisable to obtain a sample of crystal violet identified by analytical means, and to study its behavior in sulfuric acid.

Results

The spectrum of crystal violet in concentrated sulfuric acid is shown in Fig. 1. The spectrum is analogous to other triphenylcarbonium ion spectra studied by Newman[1] and by Branch[2]; both the wave lengths of maximum absorption and the value of the extinction coefficients at maximum absorption are comparable. The color of the solution was orange-brown in agreement with Newman's observations.

An identical spectrum was obtained for the methyl ether of crystal violet.

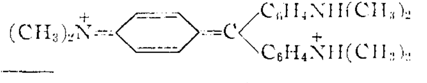
It has been shown[5] that a solution of triphenylcarbonium ions in sulfuric acid reacts immediately with methanol to form the corresponding methyl ether, according to the equations

$$(C_6H_5)_3C^+ + CH_3OH \longrightarrow (C_6H_5)_3C\overset{+}{H}OCH_3$$

$$(C_6H_5)_3C\overset{+}{H}OCH_3 + H_2O \longrightarrow (C_6H_5)_3COCH_3 + H_3O^+$$

The ordinary acid-catalyzed etherification of triphenylcarbinol or similar hindered alcohols, as well as bisulfates of the type proposed by Branch, would be expected to give practically no ether in a short reaction time. A solution of crystal violet in concentrated sulfuric acid gave the methyl ether in approximately 50% yield for a reaction time of not more than 5 minutes. This is an excellent confirmation of the assumption that the solution contained carbonium ions.

The above data support the original conclusion of Newman that only two dimethylamino groups of crystal violet are protonated in sulfuric acid, and the resulting species is a carbonium ion. Newman also suggested that the electron distribution in this ion was represented more accurately by the quinoid structure



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[1] M. S. Newman and N. C. Deno, THIS JOURNAL, **73**, 3644 (1951).

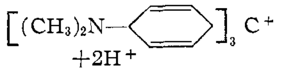
[2] G. Brauch and H. Walba, *ibid.*, **76**, 1564 (1954).

[3] A solution of 2 parts acetic acid and 98 parts concentrated sulfuric acid.

[4] A. Kovache, *Ann. chim.*, [9] **10**, 247 (1918).

[5] H. A. Smith and R. J. Smith, THIS JOURNAL, **70**, 2400 (1948).

than by the usual carbonium ion structure



The rapid formation of the ether suggests that the latter formulation is of considerable importance.

Experimental

The spectra were run on a Beckman model DU spectrophotometer; 1-cm. thick quartz cells were used.

Crystal Violet Preparation.—The carbinol was prepared by dissolving the chloride salt of crystal violet (a product of the National Aniline Division, Allied Chemical and Dye) in water and precipitating the carbinol by addition of solid sodium hydroxide pellets. After filtration, the solid carbinol was blue in color. Attempts to purify the product by recrystallization from ligroin and benzene were futile. The method of purification was that followed by Heertjes, *et al.*,[6] who also reported that simple recrystallization from organic solvents failed. The carbinol was dissolved in acetone and precipitated by the slow addition of an aqueous sodium hydroxide solution. The carbinol, collected by filtration, was much less colored than originally. Repetition of this process several times yielded a white solid. In order to remove traces of sodium hydroxide from the carbinol, it was dissolved in a small volume of anhydrous ether, and the solution filtered. The carbinol, after evaporation of the ether, was stored under vacuum since exposure to air causes the compound to turn blue slowly. The compound melted at 200° dec.; a melting point of 205° has been reported.[6]

Anal. Calcd. for $C_{25}H_{31}ON_3$: C, 77.08; H, 8.02. Found: C, 77.02; H, 8.11.

Methyl Ether Preparation.—A 3-g. sample of crystal violet was dissolved in 10 ml. of concd. sulfuric acid, giving an intense orange-brown solution. This solution was added dropwise to 50 ml. of absolute methanol which was cooled in a Dry Ice-acetone-bath during the addition. The resulting solution was immediately added to 200-300 ml. of an ice-water mixture and sufficient sodium hydroxide solution added to make the solution basic. The methyl ether was extracted from this solution with two 100-ml. portions of ether. Evaporation of this solution yielded a blue solid which was purified in the same manner as that described for the carbinol. The yield of crude material was approximately 50%. The purified ether melted with decomposition at 145-150°.

Anal. Calcd. for $C_{26}H_{33}ON_3$: C, 77.38; H, 8.24. Found: C, 77.16; H, 8.19.

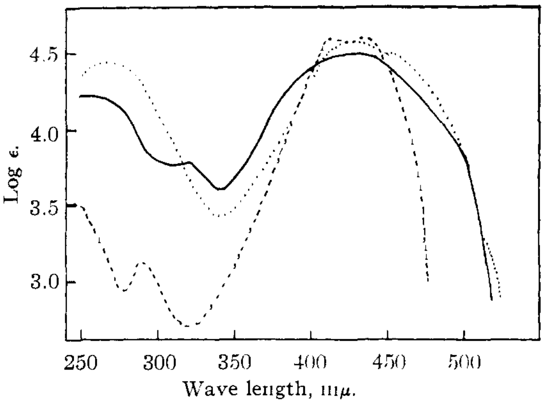


Fig. 1.—Absorption spectra of triphenylcarbonium ions in H_2SO_4: —, tri-*p*-dimethylaminophenylcarbinol; ...., tri-*p*-nitrophenylcarbinol[1]; - - - -, triphenylcarbinol.[1] Crystal violet solution was 2.5 × 10^{-5} *M*. Spectrum for methyl ether of crystal violet was identical with that for crystal violet.

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[6] P. M. Heertjes, J. C. Van Kerkhof and K. A. De Vries, *Rec. trav. chim.*, **62**, 737 (1943).

COMMUNICATIONS TO THE EDITOR

TRACER STUDY OF THE OXYGEN IN PRECIPITATED HgO AND Ag_2O; O^{18} ISOTOPE EFFECT IN THE REACTION OF OH^- WITH Hg^{++} AND Ag^+

Sir:

O^{18} experiments have been used to investigate the source of the oxygen in HgO and Ag_2O precipitated by OH^-. Further, an O^{16}/O^{18} effect was found in the reactions of Hg^{++} and Ag^+ with OH^-; O^{16} concentrates preferentially in the precipitated oxide.

Tracer experiments were as follows. One ml. of a solution of *M* NaOH, enriched in O^{18} (1.4 atom %) was added to 100 ml. of *ca.* *M* $Hg(NO_3)_2$ in normal water (0.20 atom % O^{18}); the precipitated HgO was washed, dried and pyrolyzed. The O^{18}/O^{16} ratio of the liberated oxygen was 1% lower than the ratio for normal water. Thus the oxygen in the HgO is derived exclusively from the original aquo-cation, which apparently exchanges only slowly with solvent water. Proton transfer from hydrate water to OH^- is a satisfactory explanation. However, in similar experiments with $AgNO_3$ (1-9 *M*), the Ag_2O was found to be substantially enriched in O^{18}, ranging from 0.67 atom % (no stirring, high $[Ag^+]$) to 0.26 atom % (vigorous stirring, low $[Ag^+]$).[1] A reason for the difference between Hg^{++} and Ag^+ may be the tighter binding of the coördinated water around the more polarizing Hg^{++}.[2]

The O^{16}/O^{18} isotope effect was studied with normal O^{18} abundance materials. Oxygen from the pyrolysis of the oxides was compared mass spectrometrically with reference oxygen which differed by +2.3% in O^{18}/O^{16} ratio from distilled water. Fractionation factors with respect to water were computed: $\alpha = (O^{16}/O^{18})_{\text{oxide}}/(O^{16}/O^{18})_{\text{water}}$.

When a solution of Hg^{++} was added to a solution containing excess OH^-, α was 1.018. For the

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[1] Auxiliary experiments showed negligible exchange between water and HgO or Ag_2O in 1 hr.

[2] H. Taube, *et al.* (discussed in *J. Phys. Chem.*, **58**, 523 (1954)) studied exchange between hydrated cations and solvent water and found differences in lability for various (other) cations.