of water), and trifluorolactic acid or sodium trifluorolactate (1–40 mg in 0.1 ml phosphate buffer). Readings were taken at 15-second intervals in the spectrophotometer at 340 mμ to follow the appearance of DPNH but no oxidation of substrate occurred over a 30-minute period. When sodium *dl*-lactate (2.2 mg in 0.1 ml of phosphate buffer) was substituted for trifluorolactate, DPNH appeared at an initial rate of 0.05 optical density units per 15 seconds and the addition of varying amounts of trifluorolactate (1–40 mg) did not influence the rate of oxidation.

The reduction of pyruvate to lactate was carried out by the addition to a cuvette of 0.1 *M* phosphate buffer, pH 7.4 (2.7 ml), lactic dehydrogenase (5γ in 0.1 ml of buffer), DPNH (0.3 mg in 0.1 ml of water), and sodium pyruvate (0.55 mg in 0.1 ml of buffer). Readings at 340 mμ showed an initial decrease of 0.2 optical density units per 15 seconds. The addition of up to 10 mg of sodium trifluorolactate in buffer solution, previous to the addition of sodium pyruvate, did not inhibit the reduction of pyruvate.

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CARBONIUM PERCHLORATES IN CHLOROFORM SOLUTION

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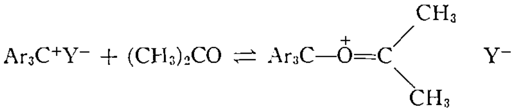
In connection with other work on the spectra of carbonium ions, we have examined the behavior of triarylmethyl perchlorates in chloroform solution. The lowering in the apparent degree of ionization (1–12) of triarylmethyl salts dissolved in organic solvents has been the subject of some speculation. Several reactions might occur, including: (*a*) repression of the ionization of carbonium salts in the organic medium (1) (eq. [1]); (*b*) co-ordination of the carbonium ion with a solvent molecule, for example ether (4, 12) or acetone (7) (eq. [2]); and (*c*) solvolysis reactions (10) which would include both the reaction of the carbonium ion with an organic solvent molecule, for example nitromethane (9) (eq. [3]), and hydrolysis to the carbinol by traces of water remaining in the imperfectly dried solvents (11) (eq. [4]).

$$Ar_3C^+Y^- \rightleftharpoons Ar_3C{-}Y \qquad [1]$$



$$Ar_3C^+Y^- + (CH_3)_2CO \rightleftharpoons Ar_3C{-}\overset{+}{O}{=}C(CH_3)_2 \quad Y^- \qquad [2]$$

$$Ar_3C^+Y^- + CH_3NO_2 \rightarrow Ar_3CCH_2NO_2 + HY \qquad [3]$$

$$Ar_3C^+Y^- + H_2O \rightleftharpoons Ar_3C{-}OH_2{}^+Y^- \rightleftharpoons Ar_3COH + HY \qquad [4]$$

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We have examined chloroform as a solvent since it is unlikely to co-ordinate with carbonium ions. Unlike carbon tetrachloride, however, it will dissolve reasonable amounts of carbonium salts.

EXPERIMENTAL

Solvents

Reagent grade chloroform was washed with 95% sulphuric acid followed by repeated washings with distilled water and was then dried over $CaCl_2$ and P_2O_5. Distillation under nitrogen from Drierite through a 30-cm fractionating column yielded a fraction which was stored in a dark bottle under nitrogen over anhydrous potassium carbonate. The bottle was equipped with a drying tube and a siphoning arrangement. Partially dried solvents were prepared in the same manner but were dried for shorter periods. "Wet" chloroform was prepared by saturating this material with water at 10°. Its water content was estimated from solubility data to be $3.5\times10^{-2}\ M$.

Reagents

Triphenylmethyl perchlorate and tris-*p*-methoxyphenylmethyl perchlorate were prepared essentially as described by Hofmann and Kirmreuther (13). Tri-*p*-tolylmethyl perchlorate was prepared by the addition of perchloric acid and dry ether to an acetic anhydride solution of the carbinol. The product was recrystallized from acetic anhydride – ether and freed from solvent under vacuum. Titration with standard potassium hydroxide gave a molecular weight of 389; calculated, 384. Tri-*p*-tolylcarbinol was prepared by the Grignard reaction of *p*-tolylmagnesium bromide on di-*p*-tolyl ketone. The crude product was purified through the chloride which was then hydrolyzed by sulphuric acid to the carbinol. Recrystallization from petroleum ether gave the product, m.p. 94–96°.

Measurements

A sample of the perchlorate (5–15 mg) was weighed into a dry volumetric flask and dissolved in acetic anhydride. Aliquots (0.05–0.5 ml) of this solution were transferred to 5-ml volumetric flasks and evaporated to dryness under vacuum. Dry air was then admitted to the flask. The succeeding operations of filling the flask with solvent and then filling the glass-stoppered absorption cells with solvent were carried out in a dry box. Light absorption measurements were made on a Beckman DU or a Cary, Model 14 spectrophotometer. Since the color intensities in the chloroform were temperature dependent (except for the *p*-methoxy compound) the cell compartment was kept at 25.0±0.2°. Optical densities of more-concentrated solutions were measured using 0.1-cm cells. A very rapid initial partial fading, which could not be followed, occurred with the tri-*p*-tolyl and triphenyl compounds. This was followed by a slow fading reaction which obeyed exact second-order kinetics. This was corrected for by extrapolation to zero time.

RESULTS

The absorption spectra of the triarylmethyl perchlorates in chloroform in the visible region were very similar to those obtained in 50–70% sulphuric acid* except that the absorption maxima were shifted from 2–8 mμ to the red. The quantity $D_{\lambda_{\max}}/\int Dd_{\lambda}$, the

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**We have observed that the carbonium ion spectrum for each of these compounds is altered in more-concentrated sulphuric acid. These changes, which are still being investigated, become marked in regions above 80%, 100%, and 102% sulphuric acid for tris-p-methoxyphenylmethyl, tri-p-tolylmethyl, and triphenylmethyl cations, respectively, and may account for some of the discrepancies in carbonium ion spectra reported in the literature.*

optical density at the wavelength maxima divided by the area under the curve, was identical to within 2% in sulphuric acid and chloroform.

The variation of optical density with concentration of dissolved salt is shown in Fig. 1

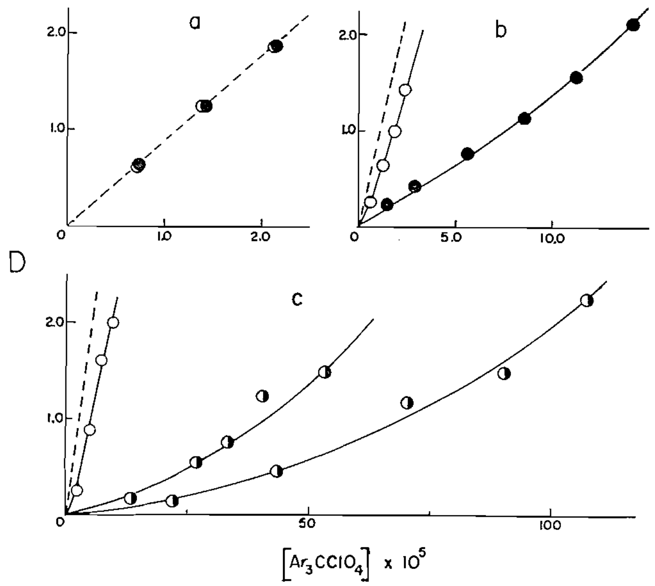


FIG. 1. Variation of optical density with molarity of dissolved triarylmethyl perchlorate. (*a*) $(p\text{-}CH_3OC_6H_4)_3C^+ClO_4^-$, (*b*) $(p\text{-}CH_3C_6H_4)_3C^+ClO_4^-$, (*c*) $(C_6H_5)_3C^+ClO_4^-$; ○ dry $CHCl_3$, ◑ partially dried $CHCl_3$, ● wet $CHCl_3$; the broken line corresponds to the extinction coefficient found for the carbonium ions in H_2SO_4 (Table I).

TABLE I

Spectral data for carbonium perchlorates

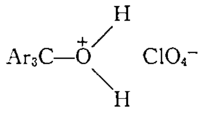
Tris-*p*-methoxyphenol			Tri-*p*-tolyl			Triphenyl		
Solvent	λ_{max} (mμ)	$\epsilon \times 10^{-4}$	Solvent	λ_{max} (mμ)	$\epsilon \times 10^{-4}$	Solvent	λ_{max} (mμ)	$\epsilon \times 10^{-4}$
56.8% H_2SO_4	484	8.8	83.0% H_2SO_4	452	9.0	96.0% H_2SO_4	433	3.8
$CHCl_3$	492		$CHCl_3$	454		$CHCl_3$	435	

for the three carbonium perchlorates dissolved in both "dry" and "wet" chloroform. It can be seen that the ionization of tris-*p*-methoxyphenylmethyl perchlorate is complete in both wet and dry chloroform and that hydrolysis of this highly resonance stabilized carbonium ion does not proceed to a measurable extent. (The excellent agreement in Fig. 1*a* between the experimental points for chloroform solution and the line for 56.8% sulphuric acid may be fortuitous since a somewhat *higher* extinction coefficient has been reported for this ion in nitrobenzene (3).)

Tri-*p*-tolylmethyl perchlorate and triphenylmethyl perchlorate both show a reduction in the concentration of carbonium ion, particularly the triphenyl compound in the partially dried solvent (Fig. 1*c*). A wet chloroform solution of the latter could not be studied since a turbid solution resulted when sufficient perchlorate was used to produce a measurable color. The difficulty in obtaining reproducibly "dry" samples of chloroform precludes any exact comparison between the three perchlorates in the dried and partially dried solvents.

Since all the triarylmethyl perchlorates are highly colored in the solid state, it is generally believed that covalent forms of these compounds are unimportant. The approach, in the present cases, to complete ionization, which accompanies rigorous drying of the solvent is in accord with this. The slow fading of the carbonium ion color may be due to a solvolysis reaction corresponding to eq. [3] or to ether formation, but it seems unlikely that the very fast initial decrease in color could be due to this. We believe, in fact, that the latter effect is due to the rapid hydrolysis of the carbonium perchlorate ion pair by the small amount of water present and that the curves in Fig. 1 are explained by the equilibria shown in eq. [4]. (Traces of acid present in the chloroform would reverse these reactions but we believe that acids are absent since prolonged treatment with anhydrous potassium carbonate always *increased* the apparent extinction coefficient.)

There are several possible structures for the colorless hydrolysis product, and their relative concentrations should depend on the amount of water present.



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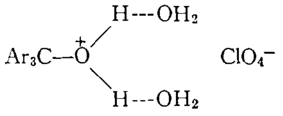

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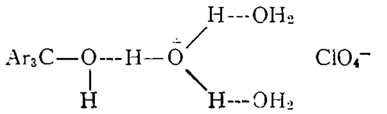

III

$Ar_3COH + H_9O_4^+ClO_4^-$

IV

Specific solvation effects such as those shown above involving hydrogen bonding (14, 15) will be most important in the low dielectric solvent chloroform. With a limited amount of water it seems likely that I would be formed whereas in the wetter solutions the carbinol would be expected to become less and less important in the dispersal of the positive charge. That is, the ion pairs II, III, and eventually IV, the carbinol plus the normal hydrated form of perchloric acid (16, 17), should become the principal cations in solution.

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THE POLARIZATION OF THE FLUORESCENCE OF 1- AND 2-NAPHTHOIC ACID[1]

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The naphthoic acids have received considerable spectroscopic attention within recent years. Weller (1) and, more recently, Porter and Jackson (2) have determined pK values for the lowest excited states of the molecule. Kasha and El Bayoumi (3) have measured solvent spectral shifts in solution. Hochstrasser examined the fluorescence and phosphorescence spectra in various solvents (10).

Porter and Jackson concluded that excitation to the lowest excited singlet level of the acids involves an orbital promotion of the type $n \longrightarrow \pi^*$. This conclusion was based on the vastly different pK values for the molecule in its ground and first excited singlet state. The large difference in pK (pK^* − pK = 8 units) quoted by these authors applies to the protonated acid – acid equilibrium and not, as stated, to the acid–anion equilibrium (1). The value of ΔpK for the anionic system is about 2–4 units (5). Therefore the conclusions regarding the orbital nature of the lowest excited singlet level are not convincing.

On the basis of absorption intensity and solvent effects, El Bayoumi and Kasha assumed that the first excited singlet state is of π,π^* character, for which only slight changes of acid strength would be predicted.

Absorption spectra need not always provide proof of the character of the *lowest excited level* of a molecule. If absorption to this state is very weak, as for example would be the case for an $n \longrightarrow \pi^*$ transition, a nearby strong transition, e.g. $\pi \longrightarrow \pi^*$, could mask the weak transition. This is especially true for organic acids since the absorption spectra are characteristically diffuse.

Fluorescence originates from the lowest excited singlet level for essentially all common polyatomic molecules. Thus only by means of emission studies of diffuse spectra can conclusive date be obtained for extremely weak bands which lie very close to stronger bands. In this note some results on the polarized emission spectra of thin crystals of 1- and 2-naphthoic acid are presented in order to determine the direction of the transition moment connecting the ground and emitting levels.

The crystal structures of 1-naphthoic acid (6) and of 2-naphthoic acid (7) are known and these provide the exact orientations of the molecules in the unit cell. For both acids the crystal is composed of planar dimeric units and for 1-naphthoic acid the normal to the dimer plane is nearly coincident with the crystallographic *b*-axis. Very thin (∼30 μ), microscopically perfect plates were prepared by sublimation. The crystals were mounted on quartz disks with the *b*-axis vertical and the blue fluorescence (excited by Hg 3130 Å) was observed normal to the *100* face. The emission was analyzed by a polaroid sheet

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[1] *This work was supported by a grant from the National Research Council of Canada.*