tent of the mixture could be calculated. The same batch of acetic acid–water–hydrochloric acid was used throughout this work.

This mixture (100 cc.) was pipetted into a long-necked glass-stoppered flask which was immersed in a bath at 30.00 ± 0.05°. Two 5-cc. samples were pipetted out and the chloride ion concentration of each was determined exactly as described below for samples of reaction mixture. Since the pipets were calibrated both for delivery and withdrawal, the volume of solution left in the flask was known.

A sample of the tertiary alcohol was introduced into the vessel from a weighing pipet, and the weight of the sample determined by difference in the weight of the pipet, which was also calibrated volumetrically so that the desired amount could readily be taken each time. The contents of the reaction vessel were immediately mixed by swirling. At suitable time intervals, 5-cc. samples were pipetted out and analyzed as follows.

The sample was introduced into a 250-cc. Erlenmeyer flask containing 40–50 g. of cracked ice. Two drops of phenolphthalein indicator was added, followed by rapid dropwise addition of 50% sodium hydroxide until just pink. Sulfuric acid (1 N) was added dropwise to bring the mixture just to the acid side. One cc. of half-saturated potassium chromate was added, and the mixture was titrated to the red silver chromate end-point with standard 0.1 N silver nitrate. Ice was present throughout the operation.

Suitable blanks were run on all reagents and on samples of the tertiary chloride which would be formed during the reaction. It was found that the latter hydrolyzed only to a negligible extent under the conditions of the analysis. The end-point was permanent, but not very sharp. Duplicate analyses checked within 0.2 ml. of silver nitrate solution (0.004 mole/liter of chloride).

Higher concentrations of water, hydrochloric acid or tertiary alcohol than those employed sometimes resulted in separation of phases before final equilibrium.

Olefin concentration was determined by treating 5-cc. samples with excess of 0.1 N bromine in carbon tetrachloride. After one minute, 10 cc. of potassium iodide solution (20%) and 50 cc. of water were added. The liberated iodine was titrated with standard 0.1 N sodium thiosulfate solution. The same values were obtained when a given sample was allowed to react with the bromine for ten minutes. There was no reaction of bromine with the tertiary alcohols or chlorides under these conditions. Duplicate analyses agreed within 0.003 mole/liter of olefin.

Test for Esterification.—One of the runs in which cyclohexyldimethylcarbinol was a reactant was arrested at a point representing 50% completion with respect to tertiary chloride formation. A sample (10 cc.) was neutralized with sodium hydroxide just as described for the chloride ion analysis, then extracted with ether. The ether layer was washed with water until the washings were no longer acid to phenolphthalein, and the ether was evaporated and the residue refluxed 24 hours with excess 10% sodium hydroxide in alcohol. The mixture was then made strongly acid with sulfuric acid and distilled until nearly dry. The distillate was analyzed both for chloride ion and total acidity. The values were identical (milliequivalents) indicating that no acetic acid had distilled, and therefore that the sample had contained no ester.

Tertiary Chloride Solvolysis Rates.—The method was essentially that of Hughes and Ingold.[4] The aqueous ethanol used had $d^{25}{}_4$ 0.8449 (about 78% ethanol, w./w.). The details of manipulation are well described, as is the method of analyzing isomer mixtures, by Brown and Silber.[5]

NEWARK, DELAWARE

[CONTRIBUTION FROM HICKRILL CHEMICAL RESEARCH FOUNDATION]

The Cycloheptatrienylium (Tropylium) Ion

BY W. VON E. DOERING[1] AND L. H. KNOX

RECEIVED APRIL 8, 1954

Thermal elimination of hydrogen bromide from dibromotropilidene produces cycloheptatrienylium bromide, the structure of which follows from its salt-like character, its hydrogenation to cycloheptane and its conversion by phenyllithium to 7-phenylcycloheptatriene. This stable cation is the parent of a new aromatic system which has been foreshadowed theoretically by the molecular orbital treatment of aromatic character and experimentally by the behavior of tropone, tropolone and azulene.

From the first generalization of six affinities due to Armstrong, von Baeyer and Bamberger,[2] to the present state of quantum mechanical foundation invented by Erich Hückel,[3] the theory of aromatic character has ascribed relative stability to those conjugated unsaturated cycles having six (π) electrons in a ring. The earliest attempts to test the theory centered about the hypothetically non-aromatic molecules, cyclobutadiene, $(CH)_4$,[4] and cycloöctatetraene, $(CH)_8$.[5] To date no results of theoretical significance have been forthcoming. Cyclobutadiene has resisted all efforts at synthesis and in any event would have a large, obscuring, angular strain; and cycloöctatetraene, although it has been synthesized, has a non-planar structure[6] and in consequence is impertinent to the theory.

With the five- and seven-membered rings, $(CH)_5$ and $(CH)_7$, the theoretical predictions[3,7,8] are definite: $(CH)_5^-$ should be more stable than $(CH)_7^-$ whereas $(CH)_7^+$ should be relatively much more stable than $(CH)_5^+$.[9] Experimental verification of these predictions is partial and incomplete. The well-known, remarkable acidity of cyclopentadiene[10,11] is to be compared with the failure to effect condensation with or form salts from cycloheptatriene.[12,13] One of the two anions has been prepared, therefore, and its properties are in accord with theory. In the positively charged series, neither $(CH)_5^+$ nor $(CH)_7^+$ has been prepared, but it can be inferred from the failure of cyclopenta-

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[2] For a discussion and references, see W. Hückel, "Theoretische Grundlagen der organischen Chemie," Vol. I, 5th Ed., Akademische Verlag, Leipzig, 1944, pp. 507–524.

[3] (a) E. Hückel, *Z. Physik*, **70**, 204 (1931); (b) "Grundzüge der Theorie ungesättigter und aromatische Verbindungen," Verlag Chemie, Berlin, 1938, pp. 71–85.

[4] R. Willstätter and W. von Schmaedel, *Ber.*, **38**, 1992 (1905).

[5] R. Willstätter and E. Waser, *ibid.*, **44**, 3423 (1911).

[6] I. L. Karle, *J. Chem. Phys.*, **20**, 65 (1952).

[7] G. W. Wheland, *ibid.*, **2**, 474 (1934).

[8] J. L. Franklin and F. H. Field, THIS JOURNAL, **75**, 2819 (1953).

[9] The resonance energies given by E. Hückel[3] for the species in terms of β follow: $(CH)_5^-$, 2.48; $(CH)_7^-$, 2.12; $(CH)_7^+$, 3.00; $(CH)_5^+$, 1.24.

[10] J. Thiele, *Ber.*, **33**, 666 (1900).

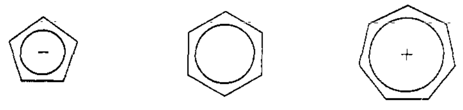
[11] Potassium *t*-butoxide (pK_a 19) converts cyclopentadiene quantitatively into its potassium salt (R. S. Rouse, Yale Univ., unpublished).

[12] J. Thiele, *Ann.*, **319**, 226 (1901).

[13] E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, THIS JOURNAL, **61**, 1057 (1939).

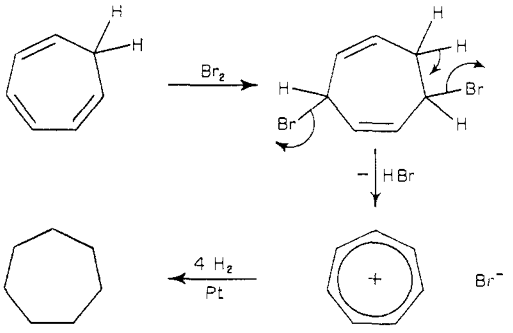
dienone to exist contrasted with the stability and basicity of cycloheptatrienone that the theoretical predictions may be correct.[14,15] Clearly three presently unknown ionic species have to be prepared and studied for a complete examination to be possible.

More modestly the theory predicts that the immediate lower and higher homologs of benzene shall constitute, along with benzene, a triad, $(CH)_5^-$ $(CH)_6$ and $(CH)_7^+$,[16] possessing aromatic resonance energy and consequently remarkable stability.



The full realization of this prediction awaits only the preparation of the third member of the series, the cycloheptatrienylium cation. It is with the preparation of this ion and a preliminary study of its properties that this paper is concerned.

When tropilidene (the detailed structure is unresolved[18,19]) is treated with one equivalent of bromine, a liquid dibromide is obtained,[20] which can be purified by distillation at 0.5 mm. and 70° but only at the expense of partial loss of hydrogen bromide and the production of a mass of crystals.[21] This material can be recrystallized from absolute ethanol to give yellow prisms which become amorphous on drying. The material, C_7H_7Br, m. p. 203°, is strongly deliquescent, miscible with water and insoluble in the organic solvents of low polarity. Catalytic hydrogenation in acetic acid leads to the uptake of four molar equivalents of hydrogen and the formation of cycloheptane. There is an instantaneous precipitation with aqueous silver nitrate.



Cycloheptatrienylium (tropylium) bromide is the only structural hypothesis consistent with our interpretation of the facts: that the high melting point, deliquescence and miscibility with water, and immediate precipitation of silver bromide indicate a salt of bromide ion; and that both the hydrogenation to cycloheptane and the formation from tropilidene by addition of bromine and removal of hydrogen bromide[22] indicate a seven-membered carbon ring.

The infrared spectrum of tropylium bromide, given in Table I, is remarkably simple showing only four bands of reasonable intensity. This simplicity is certainly consistent with the high symmetry hypothesized for the tropylium ion and is to be compared with the spectra of the isomeric bromo- and chlorotropilidenes which are much more complicated showing at least twelve bands of reasonable intensity.[23]

In the base, water, the tropylium cation behaves as a Lewis acid and is in equilibrium with the covalently bonded carbinol and an hydronium ion.

$$C_7H_7^+ + 2H_2O \rightleftharpoons C_7H_7OH + H_3O^+$$

To a first approximation the equilibrium constant is equal to the hydrogen ion concentration at the half-neutralization point and can be determined easily by potentiometric titration. The value at 25° is $K = 1.8 \times 10^{-5}$ which indicates that the tropylium ion is about as strongly acidic as acetic acid when water is the reference base.

The ultraviolet spectrum of the tropylium ion can be obtained in water only at low *p*H as was to be expected. At high *p*H the spectrum corresponds to that of 7-hydroxycycloheptatriene (tropyl alcohol) and at intermediate acidity to mixtures. Tropylium ion has λ_{min} 247 (log ϵ 3.06) and λ_{max} 275 (log ϵ 3.64), whereas the carbinol has λ_{min} 222 (log ϵ 3.37) and λ_{max} 251 (log ϵ 4.00). The yellow color of the cation is due to long tailing and not to a discrete maximum like that shown by the conjugate acids of azulenes (λ_{max} 350–370) for which a vinyltropylium structure has been proposed.[24]

By dissolving tropylium bromide in ethanol, passing in hydrogen chloride and precipitating with ether, tropylium chloride is obtained which is even more deliquescent than the bromide. When an aqueous solution of the bromide is treated with sodium carbonate, a mixture of carbinol and tropyl ether is obtained. Treatment of the ether with hydrogen bromide in ether regenerates the bromide. In a similar reaction methoxide ion converts the tropylium ion to tropyl methyl ether. This ether likewise has the properties of a covalently bonded substance and can be reconverted to the tropylium ion.

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[14] H. J. Dauben and H. J. Ringold, This Journal, **73**, 876 (1951).

[15] W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).

[16] Each member of the series has a system of hybridized p-orbitals containing six electrons, the first being formally derived from benzene by removing a $(CH)^+$ nucleus and the last by adding one. These systems are conveniently represented by the notation proposed earlier (footnote 12).[17]

[17] W. von E. Doering and L. H. Knox, This Journal, **74**, 5683 (1952).

[18] W. von E. Doering and L. H. Knox, *ibid.*, **72**, 2305 (1950).

[19] R. Willstätter, *Ann.*, **317**, 204 (1901).

[20] G. Merling, *Ber.*, 3108 (1891).

[21] "Wird das ölige Dibromtropiliden im Wasserbad erhitzt, so verwandelt es sich, indem langsam Bromwasserstoff entweicht, im Laufe von einigen Stunden, in eine gebräunte, von Oel durchtränkte Krystallmasse, ein Gemenge von Benzylbromid mit einer noch nicht näher untersuchten bromhaltigen, aus Alkohol in gelben Tafeln krystallisirenden, in Aether unlöslichen Verbindung. Dieser Körper zerfliesst an der luft, vermuthlich unter Abgabe von Bromwasserstoff, so schnell und verharzt so leicht, dass es bisher nicht gelang, denselben zu analysiren. Ich vermuthe, dass die Verbindung isomer mit dem öligen Dibromtropiliden ist."[20]

[22] The formation of tropylium bromide from dibromotropilidene can be rationalized on the basis of any one of the reasonable structures for the dibromide, whether it be derived from the cycloheptatriene or norcaradiene structure for tropilidene or whether the addition of bromine be by 1,2, 1,4 or 1,6 addition. Only one of these numerous possibilities is illustrated.

[23] Bromo- and chlorotropilidene were prepared from bromo- and chlorobenzene by irradiation with diazomethane. They are liquids, completely insoluble in water, miscible with pentane and give no precipitate with aqueous silver nitrate (W. von E. Doering and J. R. Mayer, Yale University, unpublished work).

[24] L. H. Chopard-dit-Jean and E. Heilbronner, *Helv. Chim. Acta*, **35**, 2170 (1952).

With phenylmagnesium bromide, a phenyltropilidene is obtained which gives phenylcycloheptane on catalytic hydrogenation. The ultraviolet spectrum (λ_{max} 256, log ϵ 3.56) is quite distinct from the spectra of phenyltropilidenes prepared by Cope[25] (λ_{max} 232 and 284, log ϵ 4.22 and 3.98) and by us[26] (λ_{max} 236 and 290, log ϵ 4.17 and 3.80). The phenyltropilidene made from tropylium ion has a spectrum very similar to that of tropilidene itself (λ_{max} 266, log ϵ 3.62). It seems quite likely that the material has the mechanistically reasonable structure of 7-phenylcyclohepta-1,3,5-triene (or its norcaradiene analog).

The degree of stabilization of the positive charge in the cycloheptatrienylium cation is clearly very large and, in dramatic accord with the results of the molecular orbital analysis,[3] reflects an amount of resonance stabilization in the cyclic ion large enough to overcome the normal tendency of the carbon–bromine bond to be covalent. The cycloheptatrienylium ion appears as a new aromatic system in which large resonance energy originates specifically from the cyclic nature of the system. Isolation of the system lends weight to the previous proposals that the remarkable basic properties of tropolone, tropone and azulene as well as certain reactions of these molecules are to be explained by the resonance stabilization of the tropylium ion.[14,15,24,27,28]

Experimental[29]

Dibromotropilidene.—To a solution of 2.76 g. (0.03 mole) of tropilidene in 30 ml. of dry carbon tetrachloride cooled to 0° in an ice-water-bath, 5.4 g. (0.03 mole) of bromine dissolved in 20 ml. of carbon tetrachloride was added dropwise with stirring in 20 min. Removal of solvent *in vacuo* at 25° afforded dibromotropilidene in quantitative yield as a light yellow oil, n^{25}D 1.6222. Comparison of the infrared spectrum of the product so obtained with the analytical sample prepared by two evaporative distillations at 70° at 0.5 mm., n^{25}D 1.6193, showed it to be relatively pure.

Anal. Calcd. for $C_7H_8Br_2$: C, 33.4; H, 3.2; Br, 63.4. Found: C, 33.3; H, 3.2; Br, 63.5.

Cycloheptatrienylium Bromide.—Dibromotropilidene, 5.04 g. (0.02 mole) was heated at 70° at 1 mm. for 9 hr. in a tube fitted by means of a ground joint with a water-cooled condenser. The somewhat oily, greenish yellow crystalline mass was dissolved in 15 ml. of hot absolute ethanol and allowed to crystallize at −50°. Centrifugation and drying afforded 1.338 g. (39.1%) of cycloheptatrienylium bromide as yellow prisms, m.p. 198–200° dec. After one recrystallization from absolute ethanol the material decomposed sharply at 203°.

Anal. Calcd. for C_7H_7Br: C, 49.2; H, 4.1; Br, 46.7. Found: C, 49.3; H, 4.1; Br, 46.7.

Cycloheptatrienylium bromide is insoluble in ether, carbon tetrachloride, chloroform and hydrocarbon solvents. It dissolves in methyl and ethyl alcohols on warming, and is instantly soluble in cold water from which aqueous silver nitrate gives an immediate precipitate of silver bromide.

The infrared spectrum of tropylium bromide is shown in Table I. The spectrum was obtained through the courtesy of the Perkin-Elmer Corp., Norwalk, Conn., using the pressed potassium bromide plate technique. A window of 2 mm. thickness containing a 0.2% suspension of cycloheptatrienylium bromide was used.

TABLE I

INFRARED SPECTRUM OF CYCLOHEPTATRIENYLIUM BROMIDE

Maxima		
cm.$^{-1}$	μ	Intensity absorbance
3470	2.88	0.29[a]
3095	3.24	0.18
3020	3.32	0.66
2895	3.46	0.21
1632	6.13	0.15
1482	6.75	>3.0
1388	7.21	0.11
1263	7.91	0.15
1227	8.16	0.16
1213	8.24	0.16
1118	8.95	0.15
1048	9.55	0.14
988	10.12	0.07
678	14.73	0.45
651	15.38	0.45

[a] This band almost certainly is due to water.

Hydrogenation of Cycloheptatrienylium Bromide.—Cycloheptatrienylium bromide, 0.383 g., was hydrogenated in 10 ml. of glacial acetic acid over 50 mg. of platinum oxide, four molar equivalents of hydrogen being absorbed in 80 min. Following filtration of the catalyst and dilution of the filtrate with 20 ml. of water, the hydrocarbon was extracted four times with 5-ml. portions of pentane. The extract was dried over anhydrous calcium chloride and concentrated by distillation of the pentane to a less volatile residue which was distilled from an Emich tube to give colorless cycloheptane, n^{25}D 1.4420, having an infrared spectrum identical with that of a sample of pure cycloheptane, b.p. 118°, n^{25}D 1.4423, similarly prepared by hydrogenation of pure cycloheptene, b.p. 113°, n^{25}D 1.4562.

Reaction of Cycloheptatrienylium Bromide with Phenyllithium.—To a suspension of 1.346 g. (0.0079 mole) of cycloheptatrienylium bromide in 30 ml. of dry ether a filtered ethereal solution of phenyllithium (100% excess in 50 ml. dry ether) was added dropwise with vigorous agitation in 15 min. The reaction was very mildly exothermic and gentle refluxing was briefly observed. Stirring was continued for 15 min., 20 ml. of 2 *N* hydrochloric acid added cautiously, the light yellow ethereal layer separated, washed twice with 10-ml. portions of 2 *N* sodium hydroxide followed by three washings with 15-ml. portions of water and dried over calcium chloride. Evaporative distillation of the residue remaining after the distillation of the solvent afforded a quantitative yield of the phenyltropilidene, n^{25}D 1.5867–1.5888.[30]

Hydrogenation of a solution of 0.552 g. of phenyltropilidene in 25 ml. of glacial acetic acid over 0.50 g. of 10% palladium-on-charcoal required 2.3 hr., 3 molar equivalents of hydrogen being absorbed. Evaporative distillation of the hydrogenation product, isolated as described above, afforded phenylcycloheptane as a colorless liquid, n^{25}D 1.5290 (reported[25] n^{25}D 1.5287), whose infrared spectrum was identical with that of a sample of phenylcycloheptane, n^{25}D 1.5310, prepared by hydrogenating phenyltropilidene obtained from the diazomethane ring expansion of diphenyl.

Cycloheptatrienylium Chloride.—A solution of 0.050 g. of cycloheptatrienylium bromide in 2 ml. of absolute ethanol was saturated with dry hydrogen chloride at 10°. Dry ether was added to just short of permanent turbidity and cooled to −50°. Long pale yellow needles of cycloheptatrienylium chloride crystallized, 0.022 g. (73%), m.p. 101° dec. The chloride is extremely deliquescent and slowly decomposes on storage at room temperature.

Anal Calcd. for C_7H_7Cl: C, 66.4; H, 5.6; Cl, 28.0. Found: C, 66.1; H, 5.6; Cl, 28.2.

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(25) A. C. Cope and A. A. D'Addieco, THIS JOURNAL, **73**, 3419 (1951).

(26) W. von E. Doering and L. H. Knox, *ibid.*, **75**, 297 (1953).

(27) A. C. Anderson, J. A. Nelson and J. J. Tazuma, *ibid.*, **75**, 4980 (1953).

(28) W. von E. Doering and L. H. Knox, 123rd Meeting of the American Chemical Society, Los Angeles, March 15, 1953, Abstracts of Papers, p. 8 M.

(29) All melting points are corrected. The microanalyses are by the Schwarzkopf Microanalytical Laboratory, 56-19 37th Ave., Woodside 17, New York.

(30) The mixture of phenyltropilidenes obtained by the photochemical reaction of diazomethane and diphenyl[26] had n^{25}D 1.6164–1.6213. The phenyltropilidene obtained from 2-phenyl-α-methyltropilidene methoxide has been reported to have n^{25}D 1.6202.[25]

Dicycloheptatrienyl (Ditropyl) Ether.—A solution of 0.420 g. (0.0025 mole) of cycloheptatrienylium bromide in 2 ml. of water was treated with 2 ml. of 2 *N* sodium bicarbonate solution. Carbon dioxide was vigorously evolved. The resulting turbid mixture was extracted with four 10-ml. portions of pentane, the pentane extract dried over magnesium sulfate and solvent distilled. The residue was evaporatively distilled at 100–110° at 0.5 mm. to give the ether as an almost colorless oil, 0.195 g. (81%), $n^{25}\text{D}$ 1.5735.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.8; H, 7.1. Found: C, 84.6; H, 7.0.

The ether is stable when stored under nitrogen at low temperatures but slowly darkens on standing at room temperature.

A solution of 0.050 g. of the ether in 0.5 ml. of absolute ethanol gives an immediate yellow crystalline precipitate of cycloheptatrienylium bromide when treated with dry hydrogen bromide, 0.060 g. (77%), m.p. 203° dec., unchanged in admixture with the authentic material.

7-Methoxycyclohepta[1,3,5]triene (Tropyl Methyl Ether).—To a solution of 0.513 g. of cycloheptatrienyl bromide in 10 ml. of absolute methanol, an excess of methanolic sodium methoxide was added. The colorless mixture was diluted with 25 ml. of water and extracted with four 10-ml. portions of pentane. Distillation of the solvent and evaporative distillation of the residue gave the ether as a colorless somewhat mobile liquid.

Anal. Calcd. for $C_8H_{10}O$: C, 78.6; H, 8.3; Found: C, 71.6; H, 8.2.

KATONAH, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BIRMINGHAM]

Studies of Trifluoroacetic Acid. Part X.[1] The Mechanisms of Syntheses Effected by Solutions of Oxyacids in Trifluoroacetic Anhydride[2]

BY E. J. BOURNE, J. E. B. RANDLES, M. STACEY, J. C. TATLOW AND J. M. TEDDER

RECEIVED DECEMBER 21, 1953

It is postulated that when a carboxylic acid ($R{\cdot}CO_2H$) is dissolved in trifluoroacetic anhydride, one of the components of the equilibrium mixture is the unsymmetric anhydride ($R{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CF_3$), which ionizes to a small extent into the acylium cation ($R{\cdot}CO^+$) and the trifluoroacetate anion. It is suggested that, in spite of its small concentration, the reactivity of this cation is sufficiently great for it to be responsible for the known ability of such a mixture to promote syntheses of esters and of aromatic ketones. The reactions of solutions of inorganic oxyacids in trifluoroacetic anhydride are explained similarly.

Previous papers in this series[3-6] have described syntheses which can be effected with mixtures of oxyacids and trifluoroacetic anhydride. The present communication deals with the mechanisms of these reactions, which hitherto have been discussed only briefly.[7]

We believe that, when a carboxylic acid is dissolved in trifluoroacetic anhydride, the following inter-related equilibria are established ($X = R{\cdot}CO$)

$$X{\cdot}OH + (CF_3{\cdot}CO)_2O \rightleftarrows X{\cdot}O{\cdot}CO{\cdot}CF_3 + CF_3{\cdot}CO_2H \quad (1)$$

$$X{\cdot}O{\cdot}CO{\cdot}CF_3 + X{\cdot}OH \rightleftarrows X_2O + CF_3{\cdot}CO_2H \quad (2)$$

$$X_2O + (CF_3{\cdot}CO)_2O \rightleftarrows 2X{\cdot}O{\cdot}CO{\cdot}CF_3 \quad (3)$$

Equilibrium 3 is necessarily contained in the other two equations. In addition, a small degree of ionization of the unsymmetric anhydride into X^+ and $CF_3{\cdot}CO_2^-$ is postulated. We consider that the formation of an acyl trifluoroacetate is favored by equilibria 1, 2 and 3 and that the acylium cation ($R{\cdot}CO^+$) is the principal acylating agent. The trifluoroacetic acid liberated probably assists the acylation process.

It has been known for many years[8-10] that equilibria of types 1, 2 and 3 are established in mixtures of carboxylic acids and anhydrides; Brown and Trotter[11] applied infrared absorption techniques to the analysis of such mixtures. Furthermore, there is ample evidence that acylium ions ($R{\cdot}CO^+$) are the reactive entities in many organic processes (see Burton and Praill's review[12]). Thus, the equilibria postulated above accord with analogous cases already studied; in addition, they are supported by direct evidence, both chemical and physical, which is outlined below.

Spectroscopy.—The infrared spectra of acetic anhydride and trifluoroacetic anhydride were determined in carbon tetrachloride over the range 1050–1250 cm.$^{-1}$, using a Grubb–Parsons spectrometer with a rock-salt prism. A composite curve obtained by addition of the optical densities of the two solutions was almost identical with the spectrum of a mixture of the two anhydrides, also in carbon tetrachloride, obtained within three minutes of their mutual contact. Other spectra were determined after the mixture had been kept for one hour and for 15 hours. During this time, a new absorption peak appeared at 1073 cm.$^{-1}$, at the expense of the original peaks due to the primary components; it was due almost certainly to acetic trifluoroacetic anhydride, formed according to equilibrium 3.

Cryoscopy.—The Van't Hoff factors (*i*) of trifluoroacetic acid and trifluoroacetic anhydride in acetic acid as solvent have been shown to be 1 and 2,

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(1) Part IX. J. E. B. Randles, J. C. Tatlow and J. M. Tedder, *J. Chem. Soc.*, 436 (1954).

(2) The substance of this paper was presented at the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

(3) E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, *J. Chem. Soc.*, 2976 (1949).

(4) E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, *ibid.*, 718 (1951).

(5) E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, *ibid.*, 1695 (1952).

(6) E. J. Bourne, S. H. Henry, C. E. M. Tatlow and J. C. Tatlow, *ibid.*, 4014 (1952).

(7) E. J. Bourne, J. E. B. Randles, J. C. Tatlow and J. M. Tedder, *Nature*, **168**, 942 (1951).

(8) W. Autenrieth and G. Thomae, *Ber.*, **57**, 423 (1924).

(9) A. Béhal, *Compt. rend.*, **128**, 1460 (1899); *ibid.*, **129**, 681 (1899).

(10) A. W. van der Haar, *Rec. trav. chim.*, **48**, 607 (1929).

(11) L. Brown and I. F. Trotter, *J. Chem. Soc.*, 87 (1951).

(12) H. Burton and P. F. G. Praill, *Quart. Rev.*, **6**, 302 (1952).