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Carbonium Ion Salts. V. The Spectra and Decomposition of Tropenium Halides in Methylene Chloride^{1,2}BY KENNETH M. HARMON, FRANK E. CUMMINGS,^{3a} DICK A. DAVIS^{3b} AND DENNIS J. DIESTLER^{3c}

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Tropenium halides dissolve in methylene chloride to give colored solutions; new absorption maxima are found in the visible region which are not found in more polar solvents. These bands are ascribed to charge-transfer between halide and tropenium ion, and are believed to be similar to the transitions which give rise to the colors of the solid salts. Solutions of tropenium salts in methylene chloride decompose on contact with moisture; the products are shown to be tropone, cycloheptatriene and benzaldehyde. This process is explained in terms of known reactions of the tropenium ion.

The color range shown by the solid tropenium halides (chloride white, bromide yellow, iodide red) has been attributed⁴ to charge transfer.⁵ Feldman and Winstein⁶ have demonstrated charge-transfer complexing between tropenium ion and aromatic hydrocarbons, but only one brief report⁷ had been made concerning measurements of the visible solution spectra of the halides prior to the initial report² of this work.

Tropenium salts may be divided into three general types: (1) the halides which show a range of color, sublime easily, and are not stable to the atmosphere (chloride and bromide deliquescent with decomposition,^{8,9} iodide slowly converted to the triiodide⁹); (2) a group of colorless, high-melting, air-stable salts of anions of low nucleophilicity that sublime with difficulty if at all, including the perchlorate,⁹ fluoroborate⁹ and chlorostannate,^{10,11} and (3) a group of stable, colored salts that owe their color to a complex anion as the tribromide,^{4c} triiodide⁹ and triiodomercurate.^{4c,12} The halides are unique among tropenium salts in lack of stability¹³ and in the possession of color, although neither the cation nor anion is colored.

The ${}^1E_{3u}$ band¹⁴ of tropenium ion in 96% sulfuric acid (λ_{\min} 244 (420), λ_{\max} 269(sh), 274 (4350), 279.5 $m\mu$ (3980)),¹⁵ water (λ_{\max} 275 (4350),

280(sh) $m\mu$),⁸ and acetonitrile (λ_{\max} 275 (4200), 280(sh) $m\mu$)^{4c} is not anion dependent, and at spectral concentrations (10^{-3} to 10^{-4} mole/l.) such solutions of tropenium salts are colorless unless the anion independently absorbs in the visible. Very concentrated solutions of tropenium halides in ethanol or acetonitrile are colored (bromide yellow-green, iodide red) but no discrete absorption maximum is found under the strong tailing of the tropenium peak.

Since the colors of the halides are observed only in the solid or in concentrated solutions in polar solvents, and since X-ray¹⁶ and infrared¹⁷ studies have shown that the crystalline halides are ionic, it is likely that the colors are due to a short range interaction of tropenium ion with halide ion. Such interactions could be studied in the solid, or in a solvent where ion association brings cation and anion into intimate contact. This paper reports the spectra of the colored solutions of tropenium halides in methylene chloride, and gives evidence that indicates that the origin of these colors is electron transfer from halide ion to tropenium ion. Solid state spectra are currently being investigated.

Methylene chloride proved to be an excellent solvent for these studies; it is anucleophilic and easily purified, and it dissolves tropenium salts adequately.¹⁸ With a dielectric constant of 9.08 at 25° it should theoretically¹⁹ give a high degree of ionic association. The exact extent of association is not known; we are initiating a study of the conductivity of these solutions after the manner of Fuoss and Kraus²⁰ to determine the association constants. Preliminary measurements² indicate that the bromide is a much weaker electrolyte in methylene chloride than in acetonitrile²¹ and it is reasonable¹⁹ that association is greater than 95% at the concentrations (about 1×10^{-3} mole/l.) at which our spectra were recorded. It should be pointed out, however, that epsilon values in this

(1) Supported by the Petroleum Research Fund, the National Science Foundation, and Claremont University College.

(2) Published in preliminary form in a Communication, K. M. Harmon, F. E. Cummings, D. A. Davis and D. J. Diestler, *J. Am. Chem. Soc.*, **84**, 120 (1962).

(3) (a) National Science Foundation Scholar, 1961; (b) National Science Foundation Scholar, 1960; (c) American Chemical Society, Petroleum Research Fund Scholar, 1961.

(4) (a) E. M. Kosower and P. E. Klinedinst, Jr., *J. Am. Chem. Soc.*, **78**, 3493 (1956); (b) W. von E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957); (c) H. J. Dauben, Jr., and K. M. Harmon, unpublished work reported in Ph.D. Thesis of K. M. H., University of Washington, 1958; *Dissertation Abstr.*, **19**, 1563 (1959).

(5) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950); **74**, 811 (1952).

(6) M. Feldman and S. Winstein, *ibid.*, **83**, 3338 (1961).

(7) K. M. Harmon and A. B. Harmon, *ibid.*, **83**, 865 (1961).

(8) W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

(9) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *ibid.*, **79**, 4557 (1957).

(10) D. Bryce-Smith and N. A. Perkins, *Chemistry & Industry*, 1022 (1959).

(11) K. M. Harmon, A. B. Harmon and F. E. Cummings, *J. Am. Chem. Soc.*, **83**, 3912 (1961).

(12) H. J. Dauben, Jr., and L. R. Honnen, unpublished work in Ph.D. Thesis of L. R. H., University of Washington, 1962.

(13) Tropenium chloroborate¹¹ and bromoborate⁷ are not air stable since the anions react irreversibly with water; however, both of these colorless salts are more stable than the corresponding halides.

(14) J. N. Murrell and H. C. Longuet-Higgins, *J. Chem. Phys.*, **23**, 2345 (1955).

(15) The slight difference from our previously reported values² may be attributed to higher resolution in the present data.

(16) A. I. Kitaigorodskii, Yu. T. Struchkov, T. L. Khotsyanova, M. E. Vol'pin and D. N. Kursanov, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, **1**, 32 (1960).

(17) W. G. Fateley and E. R. Lippincott, *J. Chem. Phys.*, **26**, 1471 (1957).

(18) The initial choice of methylene chloride was based, however, not on reason but on the chance observation—in the course of other work²—that tropenium bromide dissolves in this solvent to give an orange color not previously observed in other solutions.

(19) C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956), and references therein.

(20) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 21 (1933).

(21) H. J. Dauben, Jr., and F. A. Gadecki, unpublished work in Ph.D. Thesis of F. A. G., University of Washington, 1957.

TABLE I
 SPECTRA OF TROPENIUM SALTS IN VARIOUS SOLVENTS

Anion	Solvent	Soln. color	$\lambda_{\min}, m\mu$ ($^1E_{3u}Tr^+$)	$\lambda_{\max}, m\mu$ ($^1E_{3u}Tr^+$)	λ_{\min} C-T complex, $m\mu$	λ_{\max} C-T complex, $m\mu$
All	H ₂ SO ₄	None	244 (420)	269 (sh) 274 (4350) 279.5 (3980)	None	None
All	H ₂ O	None	246 (230)	275 (4350)	None	None
All	CH ₃ CN	None	246 (200)	275 (4200)	None	None
BF ₄ ⁻	CH ₂ Cl ₂	None	253.5 (785)	271.5 (sh) 278 (4270) 283 (sh)	None	None
Cl ⁻	CH ₂ Cl ₂	Yellow	249 (2380)	276 (4070)	None	298 (1820)
Br ⁻	CH ₂ Cl ₂	Orange	253 (1480)	277 (4270)	310 (660)	402 (1380)
I ⁻	CH ₂ Cl ₂	Violet	264 (3180)	278 (4270)	306 (190) 447 (1060)	422 (1120) 575 (1880)

paper have been calculated on the assumption that 100% association occurs, *i.e.*, that all of the tropenium ion in solution is paired or otherwise aggregated with halide ion.

Results.—The spectrum of tropenium fluoroborate in methylene chloride (λ_{\min} 253.5 (785), λ_{\max} 271.5(sh), 278 (4270), 283(sh) $m\mu$) is similar to that in sulfuric acid, and the solution is colorless. However, tropenium halides dissolve in methylene chloride to give colored solutions at spectral concentrations (chloride light yellow, bromide deep orange, iodide deep violet) with new absorption bands (chloride: λ_{\max} 298 $m\mu$ (1820); bromide: λ_{\max} 402 $m\mu$ (1380); iodide: λ_{\max} 422 (1120), 575 $m\mu$ (1880)) as shown in Fig. 1. In addition,

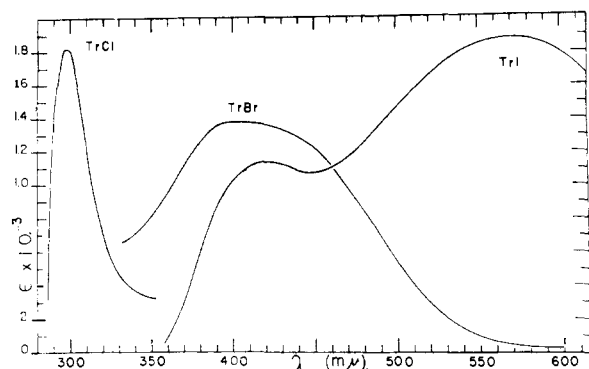


Fig. 1.—Charge-transfer spectra of tropenium halides in methylene chloride.

the tropenium ion $^1E_{3u}$ band loses its structure and shows a smooth peak with a higher minimum but almost unchanged maximum (chloride: λ_{\min} 249 (2380), λ_{\max} 276 $m\mu$ (4070); bromide: λ_{\min} 253 (1480), λ_{\max} 277 $m\mu$ (4270); iodide (see discussion below): λ_{\min} 264 (3180), λ_{\max} 278 $m\mu$ (4270)). Spectral properties of tropenium salts in various solvents are summarized in Table I.

The spectrum of tropenium bromide is recorded in a straight-forward manner (see Experimental); however, the raw data for the chloride and iodide require further treatment to yield the listed values. A discrete new maximum is not present in the spectrum of the chloride; rather, the tropenium band is built up heavily on the long wave length side, an effect not found with the other halides. We assume that this is caused by a new absorption

lying beneath the tropenium ion band, and estimate its position and intensity by subtracting from the recorded spectrum of the chloride the spectrum of a solution of tropenium fluoroborate of equivalent concentration.

The spectrum of tropenium iodide is contaminated with triiodide ion.²² This is accounted for by solving simultaneously at two wave lengths λ_1 and λ_2 equations of the form

$$(a - nx)(\epsilon_1 Tr^+) + (x)(\epsilon_1 I_3^-) = D_1$$

$$(a - nx)(\epsilon_2 Tr^+) + (x)(\epsilon_2 I_3^-) = D_2$$

where a is the initial concentration of tropenium ion and x is the concentration of triiodide ion. Epsilon values for triiodide ion were determined by recording the spectrum of tetramethylammonium triiodide in methylene chloride saturated with tetramethylammonium iodide. The ratio, but not the absolute value, of ϵ_1 and ϵ_2 for tropenium must be known; data for tropenium fluoroborate are used. The concentration of triiodide ion may then be solved for explicitly, and the absorption of that amount of triiodide ion subtracted from the recorded spectrum of tropenium iodide. This yields the shape of the tropenium iodide spectrum, but does not allow an assignment of epsilon values. We have made an arbitrary assignment of 4270 (the value shown by the bromide and fluoroborate) for (ϵTr^+) at 278 $m\mu$ in the tropenium iodide spectrum. The value of n in the foregoing equation may now be estimated, and is found to be slightly less than four. Thus processes other than simple homolysis of tropenium iodide to iodine are decreasing the tropenium ion concentration. Assumption of a value of 2 for n as required by homolysis yields an epsilon value of 3460 for tropenium ion, which is much lower than that observed in any other case.

The effects of concentration and added bromide ion on the visible spectrum of tropenium bromide were studied briefly. Over the concentration range of 2×10^{-5} to 1×10^{-3} M tropenium bromide there is little change in ϵ complex, and the spectrum is unchanged when methylene chloride saturated with tetramethylammonium bromide is used as solvent.

(22) E. M. Kosower, *J. Am. Chem. Soc.*, **77**, 3883 (1955), also encountered triiodide formation in studying the spectra of 1-methylpyridinium iodide; he avoided it by using dilute thiosulfate solution as a solvent, a route not open to us.

When tropenium fluoroborate is dissolved in methylene chloride saturated with tetramethylammonium bromide, a colored band at 402 $m\mu$ develops, and with tetramethylammonium iodide bands at 420 and 575 $m\mu$ appear. Conversion in this process does not exceed 10%; if halide does replace fluoroborate in ion-pairs to any extent, the entity formed differs from that dissolved away from a halide crystal, perhaps by inclusion of solvent. Feldman and Winstein⁶ report that addition of tetrabutylammonium bromide to tropenium fluoroborate in ethylene dichloride gives rise to tribromide ion. We find that both tetramethylammonium bromide and iodide alone give trihalide ion on standing in methylene chloride, although this effect is depressed by using recrystallized halide. However, tribromide ion is not responsible for the color of tropenium bromide solutions, since we find that solutions of preformed tropenium tribromide²³ in methylene chloride possess no maxima other than the intense band of the tribromide ion at 272 $m\mu$.

Solutions of tropenium halides in methylene chloride are relatively stable if rigorously protected from the atmosphere. Tropenium chloride solution shows no spectral change after 24 hours in a dry-box, and tropenium bromide solution shows no change in this time—and only slight decomposition in two weeks—if stored in a desiccator. When tropenium iodide is dissolved in methylene chloride in a sealed spectral cell, the solution remains violet for many hours; after 5 hours only 13% of the complex absorption at 575 $m\mu$ is lost. More concentrated solutions of the iodide remain violet for several days in a sealed flask.

There is a marked contrast in stability if these solutions are exposed to the atmosphere, or are contacted with small quantities of water. Tropenium chloride solution undergoes a rapid spectral change if opened once to the air, and the spectrum of tropenium is replaced by that of tropone; similar effects are noted if a drop of water is added. Tropone and cycloheptatriene are isolated from such solutions, in addition to unreacted tropenium ion. Tropenium bromide solutions fade rapidly if exposed to the air or contacted with water, and the products include benzaldehyde as well as tropone and cycloheptatriene. Tropenium iodide solutions turn brown immediately on exposure to the air and, in such decomposed solutions, benzaldehyde is the major new species with small amounts of tropone also present. The presence of tetramethylammonium bromide in tropenium bromide solutions greatly increases the proportion of benzaldehyde produced, and tropenium bromide dissolved in ether is converted to benzaldehyde in 76% yield.

Experimental

Eastman Kodak Co. white label methylene chloride was shaken with portions of concentrated sulfuric acid until the

(23) M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 2026 (1956), first reported the preparation of tropenium tribromide, though it was not then recognized as a tribromide salt. Its characterization is reported by Dauben and Harmon.^{46,24}

(24) H. J. Dauben, Jr., and K. M. Harmon, Abstracts, Pacific Southwest Regional Meeting of the American Chemical Society, Redlands, Calif., Oct. 25, 1958.

acid layer remained colorless, then with water, dilute bicarbonate, water again, and pre-dried overnight with calcium chloride. The solvent was then distilled from phosphorus pentoxide through a 15-inch column of stainless steel wool and stored in a brown bottle over Linde 4 A molecular sieve until used. Methylene chloride treated in this manner had a specific conductance less than 3×10^{-8} mho and did not fume when mixed with liquid boron chloride. When used for spectra, methylene chloride was redistilled from phosphorus pentoxide in an all-glass apparatus in which a quantity could be held and admitted all at once into a volumetric flask attached to the apparatus by a ground joint. Matheson acetonitrile was refluxed with and distilled from phosphorus pentoxide and stored in a brown bottle over molecular sieve. Baker and Adamson reagent grade anhydrous ether was stored over sodium wire; Baker and Adamson anhydrous methanol and U. S. I. absolute ethanol were used without further treatment. All solvents were transferred with pipet or pump. Cycloheptatriene was generously furnished by the Shell Chemical Co.; it was distilled under nitrogen to give a colorless liquid containing 10% toluene (by v.p.c.). Cycloheptatriene was stored under nitrogen at 0° until used. Eastman Kodak Co. white label tetramethylammonium halides were recrystallized from absolute ethanol. Baker and Adamson reagent grade 96% sulfuric acid was used for spectral solutions.

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Ultraviolet and visible spectra were recorded with a Cary model 13 spectrophotometer using stoppered silica cells of either 0.1 cm. or 1 cm. path length as required. The ultraviolet wave length cutoff is 221 $m\mu$ in the 0.1-cm. cells and 229 $m\mu$ in the 1-cm. cells for the methylene chloride used. Sulfuric acid is transparent to the limit of the instrument. A Mettler H-5 balance was used for routine weighings, and a Mettler H-16 was used for small quantities.

Tropenium Chloride.—The method was suggested by L. R. Honnen. All operations involving opening the reaction flask were carried out in a glove-box under nitrogen. Solvents were stored in the glove-box and transferred therein with pipet. All glassware was pre-dried in an oven and stored in the glove-box until used. The chloride was prepared in small batches such that a whole sample could be used for a single spectral determination.

A drop or so of tropenyl methyl ether (prepared by the method of Doering and Knox⁸ as a colorless liquid (ultraviolet spectrum 96% sulfuric acid²⁵ λ_{\max} 268(sh), 274 (4200), 280 $m\mu$) was dissolved in dry ether (20 ml.) in a 50-ml. glass-stoppered volumetric flask. The flask was fitted with a gas delivery head and anhydrous hydrogen chloride passed over the solution with swirling; white crystals of the chloride precipitated immediately. The ether was removed, and the precipitate washed with ether (2 \times 25 ml.) and dried *in vacuo* to give well-formed colorless needles.

To prepare a spectral solution the flask is stoppered tightly, weighed rapidly, and returned to the glove-box. Methylene chloride is added and the resulting light yellow solution transferred to a stoppered spectral cell in the glove-box; ultraviolet spectrum (methylene chloride): λ_{\min} 249 (2380), λ_{\max} 276 $m\mu$ (4070).

Tropenium Bromide.—The method is that of Dauben, *et al.*⁹ Triphenylmethyl bromide was prepared by the method of Bachmann²⁶ and was recrystallized from benzene to which a few drops of acetyl bromide had been added; the crystals so obtained were crushed and dried *in vacuo* to give a white powder, m.p. 152° (reported²⁷ 152°).

Cycloheptatriene (1.08 g., 10.6 mmoles) and triphenylmethyl bromide (3.16 g., 10.2 mmoles) were mixed in a small flask and liquid sulfur dioxide (50 ml.) added by pouring from a trap. The flask was fitted with a drying tube and sulfur dioxide evaporated by means of a gentle stream of air directed against the outside of the bottom of the flask. When the sulfur dioxide was nearly gone the material in the flask was covered with dry ether (50 ml.) and allowed to stand for 1 hour. The solid was then triturated with ether (2

(25) Dauben, *et al.*,⁹ report the spectrum of tropenium ion in this solvent as λ_{\max} 268(sh), 273.5 (4350), 280 $m\mu$. Tropenyl methyl ether is cleaved quantitatively to tropenium ion by acids.⁴⁶

(26) W. E. Bachmann, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Editor, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 841.

(27) H. Schwarz, *Ber.*, **28**, 2517 (1895).

× 50 ml.) and dried *in vacuo* to give 97.2% tropenium bromide (1.70 g., 9.95 mmoles) as a brilliant canary-yellow powder, m.p. 204° (reported⁸ 203°); ultraviolet spectrum (96% sulfuric acid):²⁵ λ_{\max} 268(sh), 274 (4360), 280 μ .

Tropenium bromide is best stored under dry ether. When a spectral sample is desired a slurry of bromide and ether is transferred to a 50-ml. volumetric flask with a dropper, the flask is fitted with a ground glass pumping head, and the bromide is dried *in vacuo* and weighed. Addition of methylene chloride gives a deep orange solution; ultraviolet spectrum (methylene chloride): λ_{\min} 253 (1480), 310 (660), λ_{\max} 277 (4270), 402 μ (1380).

Tropenium Iodide.—The method is that of Doering and Knox.^{4b} Tropenium bromide (1.61 g., 9.42 mmoles) was dissolved in absolute ethanol (75 ml.) and 48% hydriodic acid (7.3 ml.) added dropwise. An immediate red precipitate formed. The flask was cooled in an ice-bath until no more solid formed, the solution was decanted, and the iodide was washed with absolute ethanol (2 × 25 ml.) and dried *in vacuo* to give 50.2% tropenium iodide (1.02 g., 4.73 mmoles) as red micro-crystals, m.p. 128° (reported^{4b} 127°); ultraviolet spectrum (96% sulfuric acid):²⁵ λ_{\max} 268(sh), 274 (4310), 280 μ .

When spectra are desired, a small portion of the iodide is weighed in a dry 50-ml. volumetric flask, methylene chloride is added, and the flask is tightly stoppered and wrapped in foil. The flask is shaken until the crystals dissolve (a slow process). The resulting deep violet solution is transferred as rapidly as possible to a stoppered spectral cell by pipet; both cell and pipet are flushed with nitrogen before use. Spectra of such solutions are contaminated with triiodide ion absorption; when corrected for such contamination (see Discussion) the solution gives ultraviolet spectrum (methylene chloride): λ_{\min} 264 (3180), 306 (190), λ_{\max} 278 (4270), 422 (1120), 575 μ (1880).

Tropenium Tribromide.—The method is that of Dewar and Pettit.²³ Bromine (0.27 g., 1.70 mmoles) dissolved in absolute ethanol (4 ml.) was added dropwise to a solution of tropenium bromide (0.27 g., 1.58 mmoles) in the minimum amount of absolute ethanol. Yellow crystals appeared at once; these were filtered, washed on the filter with absolute ethanol, and dried *in vacuo* to give 95.6% tropenium tribromide (0.50 g., 1.51 mmoles) as yellow micro-crystals, m.p. 118° (reported^{40,23} 118°); ultraviolet spectrum (acetonitrile): λ_{\max} 271 μ (58,300); corrected for absorption of tropenium ion in acetonitrile⁴⁰: λ_{\max} 269 μ (55,000) (reported for tribromide ion in acetonitrile:²³ λ_{\max} 269 μ (55,000)). In methylene chloride the tribromide shows a single smooth peak at 272 μ (reported for tribromide ion in ethylene dichloride:²⁵ λ_{\max} 273 μ) with no other discrete maxima.

Tropenium Fluoroborate.—The method is that of Dauben, *et al.*⁹ Triphenylcarbonium fluoroborate was prepared by the method of Dauben, Honnen and Harmon.²⁹ Triphenylcarbonium fluoroborate (7.94 g., 24.1 mmoles) was covered with dry acetonitrile (20 ml.) to effect partial solution. Cycloheptatriene (3.12 g., 30.5 mmoles) was added dropwise with swirling; during this addition the remainder of the triphenylcarbonium fluoroborate dissolved and white solid began to form. After addition was complete, dry ether (25 ml.) was added to precipitate the rest of the tropenium fluoroborate and the resulting solid washed with ether (5 × 50 ml.) and dried *in vacuo* to give 97.7% tropenium fluoroborate (4.18 g., 23.6 mmoles) as snow white micro-crystals; ultraviolet spectrum (96% sulfuric acid):²⁵ λ_{\min} 244 (420), λ_{\max} 269(sh), 274 (4350), 279.5 μ (3980); (methylene chloride): λ_{\min} 253.5 (785); λ_{\max} 271.5(sh), 278 (4270), 283 μ (sh).

Tetramethylammonium Triiodide.—The method was developed from the generalized directions of Chattaway and Hoyle.³⁰ A slurry of iodine (0.80 g., 3.12 mmoles) in absolute ethanol (about 25 ml.) was added through the condenser to a refluxing, saturated mixture of tetramethylammonium iodide (0.62 g., 3.08 mmoles) in absolute ethanol (about 50 ml.). The condenser was washed with ethanol (25 ml.) to carry the last of the iodine into the reaction flask; the resulting brown solution contained no solid. The flask was fitted with a distilling head and the volume of the solu-

tion reduced to one-half by distillation of solvent. During this process iodine co-distilled, and to maintain the iodine concentration several small crystals of iodine were added to the flask during the distillation. The reaction flask was then cooled in the refrigerator overnight, and the black crystals (red by transmitted light) that formed were filtered with suction and dried on the filter to give tetramethylammonium triiodide, m.p. 117.5–118° (reported²⁰ 117°); ultraviolet spectrum in acetonitrile saturated with tetramethylammonium iodide: λ_{\max} 292 (49,300), 361 μ (26,200) (reported²³: λ_{\max} 291 (48,800), 360 μ (25,500)³¹; methylene chloride saturated with tetramethylammonium iodide: λ_{\max} 292 (44,500), 364 μ (26,300). The yield was not determined.

Decomposition Studies.—Solutions as described below were worked up by first extracting with water to remove tropenium ion, and then with 50% sulfuric acid to remove tropone (as hydroxytropenium). The remaining methylene chloride solution was then dried over calcium chloride. These three solutions were then brought to volume and analyzed by ultraviolet spectra; the following spectral values were used as standards: tropenium ion (water):³ λ_{\max} 275 (4350), 280 μ ; hydroxytropenium ion (50% sulfuric acid)³²: λ_{\max} 306 (12,300), 312 μ (sh); cycloheptatriene (methylene chloride)³³: λ_{\max} 263.5 μ (3400); benzaldehyde (methylene chloride)³³: λ_{\max} 246 (13,940), 288 (1380), 290 (sh) μ ; benzaldehyde (96% sulfuric acid)³³: λ_{\max} 296 (23,400), 336 μ (2080). In the decomposition of tropenium chloride no benzaldehyde was detected, and in the tropenium iodide case cycloheptatriene was not observed. With tropenium bromide the residual methylene chloride solution after all extractions showed mixed spectra of cycloheptatriene and benzaldehyde; the concentrations were determined by simultaneous solution at two wave lengths.

(a) Tropenium chloride (9.40 mg., 7.40 μ moles) was dissolved in methylene chloride (50.00 ml.); this light yellow solution showed λ_{\max} 276 (4070). The solution in the spectral cell (which had been exposed briefly to the atmosphere) was allowed to stand overnight; after this time it showed a new spectrum with a strong peak at 223 μ (shoulders at 229 and 233 μ) and a less intense peak at 300 μ (shoulder at 313 μ). This spectrum bore a strong resemblance to that reported for tropone.³⁴ Since the bulk of the solution (protected from the atmosphere) showed little spectral change overnight, a few drops of water was introduced, the flask thoroughly shaken, and the solution worked up as described above. Ultraviolet spectral analysis showed³⁵: (a) 29.8% (2.00 mg., 2.19 μ moles), (b) 23.8% (1.86 mg., 1.75 μ moles), (c) 33.9% (2.30 mg., 2.49 μ moles), (d) 0%, (e), 87.5%, (f) 97.6%.

(b) Tropenium bromide (27.61 mg., 161 μ moles) was covered with methylene chloride (50 ml.) and allowed to stand overnight to yield a bright orange solution, λ_{\max} 277, 403 μ . Two drops of water was added to the flask with shaking and the solution allowed to stand overnight; the undissolved bromide went into solution and the orange color was discharged. The solution now showed a high peak at 225 μ (shoulders at 228, 232 μ) and a lower peak at 298 μ (shoulder at 313 μ). After workup, ultraviolet spectral analysis showed³⁵: (a) 38.3% (5.62 mg., 61.7 μ moles), (b) 19.4% (3.32 mg., 31.3 μ moles), (c) 29.5% (3.34 mg., 47.6 μ moles), (d) 2.19% (0.23 mg., 3.53 μ moles), (e) 89.4%, (f) 99.5%.

(c) Tropenium bromide (18.90 mg., 110 μ moles) was dissolved in methylene chloride (50.00 ml.) to give an orange solution with λ_{\max} 277 ($D = 0.960$) and 401 μ ($D = 0.308$). The glass-stoppered volumetric flask was allowed to stand for 2 weeks in a desiccator; after this time the solution

(31) Popov and Swensen²⁴ list 38,800 as ϵ for the 291 peak in a table, but show the higher value on their spectral graphs.

(32) This assumes that the ϵ value for hydroxytropenium in 50% sulfuric is the same as that reported for 96% sulfuric acid.⁴⁰

(33) Determined in the course of this work using redistilled cycloheptatriene and Eastman Kodak Co. white label benzaldehyde.

(34) H. J. Dauben, Jr., and H. J. Ringold, unpublished work reported in Ph.D. Thesis of H. J. R., Univ. of Washington, 1953; they give the spectrum of tropone in ethanol as λ_{\max} 225 (25,400), 228(sh), 232(sh), 302 (7400), 312(sh) μ .

(35) (a) % recovered tropenium ion, (b) % tropone, (c) % cycloheptatriene, (d) % benzaldehyde, (e) total % recovered C₇-species, (f) total recovered C₇-species if tropone is assumed equal to cycloheptatriene.

(28) A. I. Popov and R. F. Swensen, *J. Am. Chem. Soc.*, **77**, 3724 (1955).

(29) H. J. Dauben, Jr., L. R. Honnen and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

(30) F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, **123**, 654 (1923).

was still orange and showed λ_{\max} 277 ($D = 0.858$) and 396 $m\mu$ ($D = 0.209$), with a new small peak (on the rise of the tropenium peak) at 312 $m\mu$ ($D = 0.296$). The flask was then allowed to stand in the room protected only by the glass stopper for 1 week; after this time, the color had nearly disappeared, and the solution showed λ_{\max} 277 ($D = 0.705$) and 313 $m\mu$ ($D = 0.400$) with no peak at the 400 region. After workup, ultraviolet spectral analysis showed³⁵: (a) 33.4% (3.34 mg., 36.7 μ moles), (b) 11.6% (1.36 mg., 12.8 μ moles), (c) 12.2% (1.23 mg., 13.4 μ moles), (d) 7.18% (0.84 mg., 7.90 μ moles), (e) 64.4%, (f) 65.0%.

(d) Tropenium bromide (13.2 mg., 77.2 μ moles) was dissolved in methylene chloride (50.00 ml.), which had been saturated with tetramethylammonium bromide, to give an orange solution with λ_{\max} 401 $m\mu$ (1380). The solution was allowed to stand in the glass-stoppered flask for 4 weeks; during this time the color of the solution changed to a much redder hue without significant decrease in intensity. The ultraviolet spectrum now showed an intense peak centered at 240 $m\mu$ and a weaker peak at 280–90 $m\mu$ with a shoulder at 312 $m\mu$. In the visible region, the complex peak at 401 $m\mu$ had vanished and a new absorption at 495 $m\mu$ was present. After workup, ultraviolet spectral analysis showed³⁵: (a) 0%, (b) 4.22% (0.34 mg., 3.25 μ moles), (c) not measured, (d) 39.6% (3.22 mg., 30.5 μ moles), (e) 43.8%, (f) 48.0%.

(e) Tropenium bromide (5.7 mg., 33 μ moles) was dissolved in ether (50.00 ml.) and allowed to stand overnight. An ultraviolet spectrum of the solution showed the presence of 76% benzaldehyde (2.7 mg., 25 μ moles).

(f) Tropenium iodide (30.30 mg., 139 μ moles) was shaken with methylene chloride (50.00 ml.) to effect partial solution. The solution was deep violet in color and the undissolved crystals were scarlet. The flask was allowed to stand in the room for 1 week protected only by the glass stopper; during this time it was shaken several times a day. The color changed slowly from violet to brown, and the solid dissolved gradually; the odor of benzaldehyde became apparent. The final solution was red-brown, and showed λ_{\max} 294 and 364 $m\mu$; the intensity indicated the presence of 40.3 μ moles of triiodide ion. After workup,³⁶ ultraviolet spectral analysis showed³⁵: (a) 40.4% (5.12 mg., 56.2 μ moles), (b) 6.90% (1.03 mg., 9.60 μ moles), (c) not measured, (d) 33.9% (5.00 mg., 47.2 μ moles), (e) 81.2%, (f) 88.1%.

(g) Tropenium fluoroborate (7.1 mg., 40 μ moles) was dissolved in methylene chloride (50 ml.). The ultraviolet spectrum was recorded at once, and again after the solution had stood several days protected only by the ground stopper. No discernible change took place in this time. The solution was contacted with water by stirring briefly with a damp stirring rod, and again allowed to stand. The spectrum underwent a steady change; the minimum region at 254 $m\mu$ was raised and shifted toward lower wave lengths, the tropenium peak diminished and broadened on the low wave length side, and the region from 300 to 312 $m\mu$ was raised with a shoulder developing at 312 $m\mu$. The spectrum resembled that of a decomposing tropenium chloride solution; however, the conversion to tropone and cycloheptatriene was much slower than that observed with the chloride. The relative amounts of products after 48 hours were estimated by a simultaneous solution at three wave lengths; the values obtained were³⁵: (a) 58% (2.1 mg., 23 μ moles), (b) 13% (0.6 mg., 5.3 μ moles),³⁷ (c) 15% (0.6 mg., 6.0 μ moles), (d) 0%, (e) 86%, (f) 88%.

Discussion.—We believe that the new bands giving rise to the colors of solutions of tropenium halides in methylene chloride are caused by electron or charge-transfer from halide ion to tropenium ion for the following reasons: (1) These bands are most intense in fresh solutions, and changes that occur in the solutions (see below) proceed with loss of color. Thus decomposition products do not cause the color. (2) Addition of tetramethylammonium halide to tropenium fluoro-

(36) After extraction with water and acid the methylene chloride was shaken with dilute aqueous thiosulfate solution to remove iodine.

(37) Since we possessed the qualitative but not the quantitative spectrum of tropone in methylene chloride, we assumed the epsilon values in this solvent to be the same as those reported by Ringold³⁴ in ethanol.

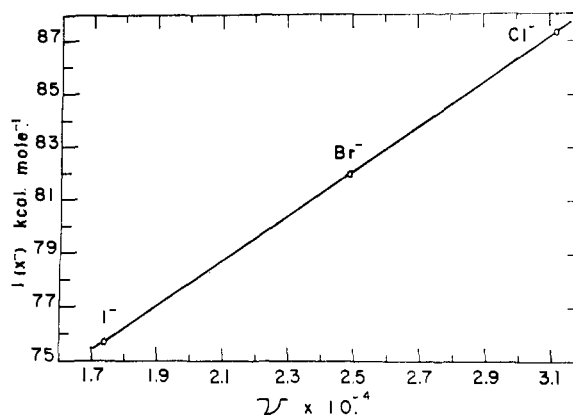


Fig. 2.—Plot of ionization potential of halide ion against energy of tropenium halide charge-transfer band.

borate in methylene chloride solution gives rise to bands identical with those of the corresponding tropenium halide. (3) For a series of charge-transfer complexes of the same acceptor with different but closely related donors the absorption bands should show a linear increase in energy with increasing ionization potential of the donor.³⁸ We find that a plot of ν in cm.^{-1} against the ionization potential of the halide ions³⁹ gives a good straight line, as shown in Fig. 2. For this plot the longer wave length peak at 575 $m\mu$ of the tropenium iodide complex was used, since this corresponds to the "normal" electron affinity of the $P_{1/2}$ state of iodine atom.⁴⁰ (4) The separation of the two bands of the tropenium iodide complex (6400 cm.^{-1}) is in reasonable agreement with that expected for the different electron affinities of the $P_{3/2}$ and $P_{1/2}$ states of the iodine atom (7200 cm.^{-1}).⁴¹ Also, the tropenium bromide and iodide charge-transfer spectra are strikingly similar in shape to the spectra of the corresponding halide ion-water complexes,⁴⁰ or to the spectra of the alkali metal halides in the vapor or solid state.⁴¹ (5) X-Ray and piezoelectric data on solid tropenium iodide¹⁶ give evidence for a weak charge-transfer bond between the iodide ion and the tropenium ion, which might be expected to persist in ion-pairs.

The decomposition of solutions of tropenium salts in methylene chloride follows two paths: (1) which produces mixtures of cycloheptatriene and tropone, and (2) which produces benzaldehyde. With tropenium fluoroborate and chloride route (1) occurs exclusively, and with the iodide (2) predominates. Both routes are operative in the case of the bromide, though changing conditions can vary the relative amounts. The decompositions appear in all cases to be initiated by water. We have interpreted these decompositions in terms of known reactions of the tropenium ion as discussed below. We have not ruled out all alternate mechanisms,

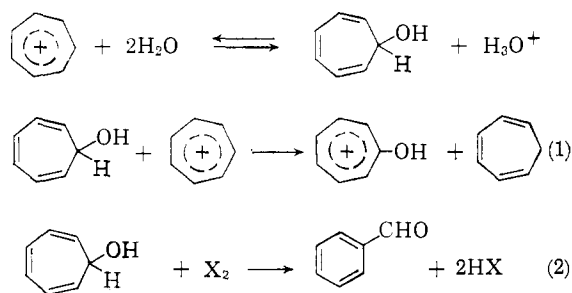
(38) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).

(39) Taken as equal and opposite to the electron affinity of the halide ions as listed in L. Pauling, "The Nature of the Chemical Bond," Third Edition, Cornell University Press, Ithaca, N. Y., 1960, pp. 510–511. Reference 8, p. 511, of this text gives 14 references to the original literature.

(40) R. Platzmann and J. Franck, *Z. Physik*, **138**, 411 (1954).

(41) E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).

but hesitate to invoke more complex explanations when simpler ones seem readily available.



The first step is the hydrolysis of tropenium ion to tropenyl alcohol and hydrogen halide, followed by (1) hydride abstraction from tropenyl alcohol by tropenium to form cycloheptatriene and tropone (*i.e.*, hydroxytropenium), and/or (2) oxidation of hydrogen halide to halogen (as trihalide ion) followed by attack of halogen on tropenyl alcohol to form benzaldehyde.

Hydride transfer between tropenium ion and a seven-substituted cycloheptatriene has been reported by Nozoe⁴² for tropenyl alcohol; Dauben,⁴³ ter Borg⁴⁴ and Vol'pin⁴⁵ for ditropenyl ether; Vol'pin⁴⁶ for deuteriocycloheptatriene; and Conrow⁴⁷ for 7-methylcycloheptatriene. The rearrangement of tropenium tribromide to benzaldehyde in the presence of water was reported by Dewar and Pettit.²³ Dauben and Harmon^{4c,24} have investigated this reaction in detail and shown it to be one of a general type of oxidative rearrangements to benzaldehyde caused by the action of molecular halogen on 7-substituted cycloheptatrienes. Thus they find that tropenium tribromide and triiodide are converted quantitatively to benzaldehyde when treated with very dilute aqueous base (to effect hydrolysis to tropenyl alcohol and to neutralize liberated hydrogen halide) and that tropenyl alcohol, tropenyl methyl ether and ditropenyl ether form benzaldehyde when treated with bromine; if dilute base is present these reactions go nearly to completion. Tropenium ion as such, however, is not rearranged, and indeed is completely inert to molecular bromine even under very strenuous conditions.^{4c,7,48,49} The extent to which benzaldehyde is formed by the decomposition of tropenium salt solutions in methylene chloride is in direct proportion to the likelihood of halogen (or trihalide ion) formation. Thus the fluoroborate and chloride do not form benzaldehyde,

(42) T. Ikemi, T. Nozoe and H. Sugiyama, *Chemistry & Industry*, 932 (1960).

(43) H. J. Dauben, Jr., and T. Pratt, private communication.

(44) A. P. ter Borg, R. van Hilden, A. F. Bickel, W. Renold and A. S. Dreiding, *Helv. Chim. Acta*, **43**, 457 (1960).

(45) M. E. Vol'pin, Z. N. Parnes and D. N. Kursanov, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, 959 (1960).

(46) Z. N. Parnes, M. E. Vol'pin and D. N. Kursanov, *ibid.*, 763 (1960).

(47) K. Conrow, *J. Am. Chem. Soc.*, **83**, 2343 (1961).

(48) H. J. Dauben, Jr., and D. L. Pearson, unpublished work reported in Ph.D. Thesis of D. L. P., University of Washington, 1955.

(49) H. J. Dauben, Jr., and K. M. Harmon, Abstracts, 134th Meeting of the American Chemical Society, Chicago, Ill., Sept. 12, 1958, p. 35-P.

the bromide yields only a small amount (unless tetramethylammonium bromide, which has been shown to form trihalide ion under these conditions, is present), and the iodide gives considerable benzaldehyde.

Whether the halogen required for the rearrangement is formed by air oxidation of hydrogen halide or by homolysis of tropenium halide may be uncertain; however, we reject the concept of homolysis playing a significant role for the following reasons: (1) tropenium halides or their solutions are stable in the absence of moisture. (2) A homolytic mechanism fails to account for the formation of tropone and cycloheptatriene. (3) The presence of ditropenyl from homolysis would yield high values for cycloheptatriene relative to tropone in the spectral analysis. This was observed in the case of the chloride and bromide with added water; however, these appeal to the authors as the instances where homolysis is least likely to occur, and indeed little or no benzaldehyde was formed in either case. (4) With tropenium iodide, where homolysis seems most likely, the yields are such that the stoichiometry of a homolytic reaction would require that 155.9% of the original tropenium ion be incorporated in the C₇-products. (5) To speak of homolysis presupposes the existence of a carbon-halogen covalent bond in the tropenium halide; physical evidence^{16,17} appears to reject such covalency for the bromide and iodide. Turner and Doering⁵⁰ have suggested that the chloride may show some covalency on the basis of heats of hydrogenation; however, as they indicate that their chloride samples may have contained considerable water, their conclusions may need re-examination in light of this present work, since the samples may also have contained both tropone and cycloheptatriene.

The equilibrium constant for the hydrolysis of tropenium ion⁸ (1.8×10^{-5} in H₂O or about 3×10^{-7} in non-aqueous solvents) would indicate that the extent of hydrolysis should be slight in these solutions; this may well account for the fact that tropenium fluoroborate reacts slowly if at all unless considerable water is present. The rapidity with which the halides decompose in solution suggests that the existence of electron-transfer complexes in these salts may increase the reactivity of the tropenium ion with water. The decreased stability of solid tropenium halides (relative to the perchlorate or fluoroborate) may also result in part from an increased reactivity with moisture caused by complex formation in the crystal.

Tropenium iodide often darkens on standing or recrystallization with an increase in iodine content^{4b,9,21}; this process is explicable in terms of the above reactions. The conversion proceeds more rapidly with finely divided samples which suggests a surface effect. The extent and rate of decomposition vary from sample to sample; we believe this reflects the amount of exposure to atmospheric moisture. We find that small quantities of cycloheptatriene and tropone can be isolated from samples that have been exposed to the atmosphere

(50) R. B. Turner, H. Prinzbach and W. von E. Doering, *J. Am. Chem. Soc.*, **82**, 3451 (1960).

and then allowed to stand until darkened in a closed flask, which indicates a hydride transfer mechanism for this decomposition.

Our studies in this area are continuing with the investigation of solid state spectra, determination

of association constants and examination of the charge-transfer spectra of substituted troponium halides.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, CALIF.]

Molecular Geometry. II. Methyl-cyclohexanes and Cycloheptanes^{1,2}

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Machine computation is applied to the calculation of the energy difference between axial and equatorial methyls on cyclohexane. A value of 1.01 kcal./mole is obtained. Similar calculations for methyl groups on various discrete conformations of the flexible cycloheptane ring are also calculated and the use of these values in delineating the conformational analysis of substituted cycloheptanes is discussed.

The energy difference between axial and equatorial substituents on cyclohexane has long been a central feature of conformational analysis. The values generally accepted for this difference vary from 1.6–2.0 kcal./mole for axial *vs.* equatorial methyl groups, derived from spectroscopic and thermodynamic considerations.⁴ The problem of calculating the energy difference² between axial and equatorial methylcyclohexane seemed to be an important one for several reasons. Firstly, since this energy difference is made up mostly of a large number of fairly minor non-bonded interactions between the differently placed methyls and the ring, it provides an especially delicate test of the efficacy of a computer approach as well as of the accuracy of the non-bonded interaction functions chosen. Secondly, of course, the computed results may be compared with reliable experimental values, and, finally, should the computer technique provide a reasonable approximation to the empirical values it might be used with some confidence to afford as well the corresponding energies of methyls on more complex rings. The latter is of particular importance in providing a semi-quantitative basis for conformational analysis in the conformationally more complex cycloheptane system.

Dissection of the problem for machine computation (see Fig. 1) involves assignment of a specific conformation to the ring and calculation of the total energy of the molecule with the methyl group attached at a given carbon, first in one orientation (*cf.* axial) and then in the other (*cf.* equatorial); subtraction then affords the desired energy difference. The choice of functions here follows the discussion in part I²; energy terms were considered to be those arising from bond angle bending, torsional strain around single bonds and non-bonded interactions between hydrogens; these are separately calculated, using the functions discussed in

part I,² and added to provide the total strain energy of the molecule. The energy so calculated is more or less meaningless in absolute terms, as it contains no assessment of bond or coulombic energies or of zero-point energies or terms for vibration and rotation of the various bonds. The exclusion of these terms is largely justified on the ground that they will cancel in any calculation of energy *differences* between closely related conformers. Nevertheless, such an approximation of second-order contributions probably puts a serious limitation on the accuracy of the values calculated. In any event the availability of empirical values for some of the energy differences so calculated can serve as a check on the validity of this approximation, as in the examples of part I.²

As the sum of the three energy terms considered here (angle bending, torsional strain and non-bonded interactions of hydrogens) was already available from the previous computations² for the parent ring itself, without added methyl, it was deemed simpler to start with this ring value and add to it the changes occasioned by attaching the methyl group. This involves adding the change in angle bending energy⁵ at the site of the new methyl, the torsional strain due to rotation (ω_M) of the methyl group around its bond to the ring, and finally the sum of the new non-bonded H–H interactions from the methyl hydrogens to the ring hydrogens and subtraction of those interactions due to that hydrogen replaced by the methyl group on the parent ring. The various H–H distances to be calculated from the methyl hydrogens A, B and C are functions of the bond angles ϕ_M , θ_2 , θ_3 , etc., and of the dihedral (torsional) angles, ω_M , ω_1 , ω_2 , etc.; the latter are given as part of the definition of the parent ring and are modified for these distance calculations to substituents (CH₃ or H) by addition or subtraction of the relevant projection angle, as μ_M , in Fig. 2.

In a general program for the computer, these interactions are all separately computed and added for each given parent ring conformation. Also, in

(1) This work was supported in part by a generous grant from the National Institutes of Health.

(2) Paper I of the series: J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

(3) Alfred P. Sloan Foundation Fellow.

(4) W. G. Dauben and K. S. Pitzer, Chap. 1 of "Steric Effects in Organic Chemistry," ed. M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956; C. W. Beckett, K. S. Pitzer and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2488 (1947).

(5) The change in angle bending strain at C₁ (Fig. 1) is computed by adding the angle strain of the present attached groups, *i.e.*, $2E\phi_M + 3E\psi_M$, and subtracting the angle strain due to the two hydrogens on C₁ in the parent ring (see Fig. 1, ref. 2).