Denigès' Reagent[9] for Isobutylene

The usual reagent for isobutylene is 63–68% sulfuric acid but this is of value only when considerable quantities of isobutylene are present. It is unreliable for the detection of traces. Denigès' reagent, essentially acidified mercuric nitrate, is not only sensitive but selective. To prepare the reagent, 20 g. of mercuric oxide was mixed with 100 cc. of water and then heated with 40 cc. of concd. nitric acid. When dissolved, the solution was diluted with 400 cc. of water.

When passed into this reagent, isobutylene gives a yellowish turbidity, the turbidity increasing with the temperature. On boiling, a heavy orange precipitate settles. We found that 1- and 2-butenes also dissolve readily in the reagent but without the formation of yellow turbidity or precipitate. Trimethylethylene does not give the test.

In a quantitative run it was found that 52 cc. (0.13 g.) of pure isobutylene produced 2.90 g. of the precipitate. For this purpose, the gas was passed into 200 cc. of reagent which, after heating, was poured into a liter of hot water. The precipitate coagulated rapidly. It was collected on a filter, washed with hot water and dried over phosphorus pentoxide. If Denigès' formula of $HgNO_3 \cdot C_4H_8 \cdot Hg_2NO_3$ were correct, only 1.81 g. of precipitate should have formed. The 2.90 g. corresponds to 4.48% by weight of isobutylene. In a similar run 0.115 g. (46 cc.) of isobutylene gave rise to 2.52 g. of precipitate, or 4.56% of C_4H_8. Whether or not this method might be extended to a quantitative determination of isobutylene cannot be stated without further data.

Non-Formation of Isobutylene.—Four hundred cc. of the butene fraction from the 600° (8.8 sec.) experiment with 1-butene was divided into equal parts, A and B. A was passed into 200 cc. of cold Denigès' reagent. No turbidity appeared in thirty minutes and none occurred after heating. Into B was admixed 0.2 cc. of pure isobutylene before performing a similar test. A slight turbidity appeared in thirty minutes. Then the solution was warmed. It assumed an opaque yellow color. On boiling, the solution cleared up with the formation of an almost imperceptible precipitate. Thus it may be concluded that no isobutylene was formed from 1-butene by pyrolysis.

Summary

The gaseous decomposition products of 1-butene and 2-butene at 500–700° were studied. 2-Butene was the more stable isomer. In both cases, especially at 650°, extensive rearrangement occurred into the other isomer. No isobutylene was produced. The ratio of low-boiling (*cis*) to high-boiling (*trans*) 2-butene (62–38) was practically unchanged during pyrolysis. More *cis* than *trans* isomer was found in the 2-butene produced from 1-butene.

Experiments are included which deal with the identification of isobutylene and butadiene. The utility of the Frey–Hepp column in the analysis of mixtures of C_4-hydrocarbons is pointed out.

EVANSTON, ILLINOIS RECEIVED JUNE 14, 1934

---

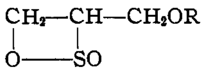
[9] Denigès, *Compt. rend.*, **126**, 1043 (1898).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reaction between Sulfur Dioxide and Olefins. Cyclohexene

BY D. S. FREDERICK, H. D. COGAN AND C. S. MARVEL

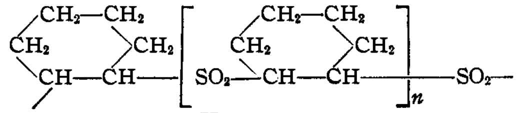
The possibility of preparing long chain molecules by the addition of sulfur dioxide to olefins has apparently been largely overlooked by organic chemists since it was first observed by Solonina[1] in a study of certain allyl ethers and related compounds. Matthews and Elder[2] obtained a patent covering resinous products prepared by the addition of sulfur dioxide to simple olefins such as ethylene, propylene and butylene. Recently Seyer and King[3] have observed that sulfur dioxide combines with cyclohexene if oxygen is present in the reaction mixture. In each of these reports the addition compounds were described as amorphous products whose empirical formulas indicated that the respective olefins had combined with sulfur dioxide in a one to one ratio. Solonina wrote a monomeric, cyclic formula (I) for his products. Matthews and Elder recognized that their products were polymeric, but did not attempt to write structural formulas for them.



$$\begin{array}{lll} CH_2 & -CH & -CH_2OR \\ | & \;\;| & \\ O & -\!\!-SO & \end{array}$$

I

Seyer and King suggested a polysulfone structure (II) for the addition product of cyclohexene and sulfur dioxide. However, they described no



II

---

[1] Solonina, *J. Russ. Phys.-Chem. Soc.*, **30**, 826 (1898); *Chem. Zentr.*, [1] 248 (1899).

[2] Matthews and Elder, British Patent 11,635 (1914); *C. A.*, **9**, 2971 (1915).

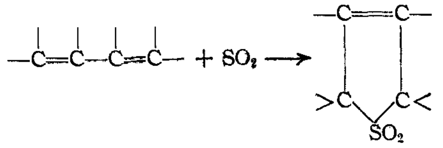
[3] Seyer and King, THIS JOURNAL, **55**, 3140 (1933).

experimental work to support this structure. In a footnote in one of his recent books, Staudinger[4] has, likewise, suggested a polysulfone structure (III) for the sulfur dioxide-ethylene addition

$$—CH_2—CH_2—[—SO_2CH_2CH_2]_n—SO_2— \quad \text{III}$$

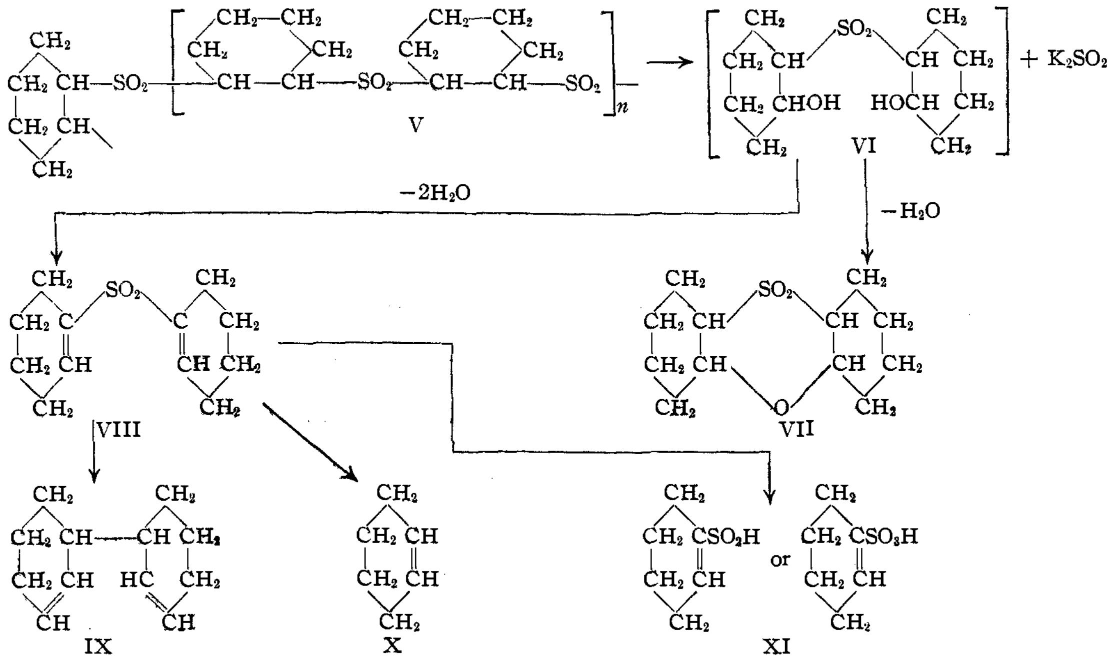
product but did not describe the work on which this structure was based.

The addition of sulfur dioxide to conjugated diene systems has been more extensively investigated. Monomeric cyclic sulfones (IV) as well as



IV

polymeric products have been obtained from cyclohexadiene, butadiene, isoprene and related compounds.[5]



In this communication we shall describe the product obtained by the addition of sulfur dioxide to cyclohexene, and show that it is a polymeric sulfone of rather high molecular weight. The addition reaction does not take place readily if the hydrocarbon is carefully freed from all traces of oxygen-containing compounds. The reaction can be catalyzed by the introduction of a small amount of 2% aqueous hydrogen peroxide. The presence of a trace of an alcohol in the reaction mixture seems to improve the yield slightly and also it improves the quality (color and stability) of the addition product. The reactants combine at room temperature to yield a white amorphous substance which is insoluble in most organic solvents. The product often becomes discolored on standing and this is more marked when all extra moisture is removed by careful drying.

Aqueous alkalies have little effect on the product in the cold. However, hot alkalies break up the polymer more or less completely, yielding cyclohexene (X), cyclohexenylsulfinic or sulfonic acid (XI), octahydrodiphenyl (IX), dicyclohexenylsulfone (VIII), dodecahydrophenoxthine dioxide (VII), potassium sulfite and other compounds which have not been identified. The formation of these products by alkaline decomposition of the addition compound gives experimental substantiation to the polysulfone structure (V) which Seyer and King[3] have suggested. The decomposition products which are given in the following chart are of the types which have been obtained in other studies of the action of alkalies on sulfones.[6]

---

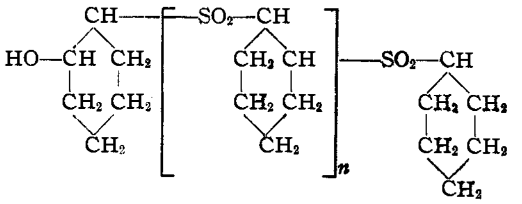
(4) Staudinger, "Die Hochmolekularen organischen Verbindungen," Verlag von Julius Springer, Berlin, 1932, page 3, footnote 4.

(5) De Brun, *Verslag, Akad. Wetenschappen*, **23**, 445 (1914); *C. A.*, **9**, 623 (1915); Hofmann and Damm, *Chem. Zentr.*, [1] 2342 (1926); Staudinger, German Patent 506,839 (1929); French Patent, 689,857 (1930); *C. A.*, **25**, 522, 3360 (1931); Eigenberger, *J. prakt. Chem.*, **127**, 307 (1930); **129**, 312 (1931); Seyer and King, This Journal, **55**, 3140 (1933); Bacher and Strating, *Rec. trav. chim.*, **53**, 525 (1934).

(6) Otto and Damköhler, *J. prakt. Chem.*, [2] **30**, 171, 321 (1884); Otto, *Ber.*, **18**, 154 (1885); **19**, 2425 (1886); Otto and Rössing, *ibid.*, **20**, 185 (1887); Fenton and Ingold, *J. Chem. Soc.*, 3127 (1928); 2338 (1929); 705 (1930).

It should be noted that the intermediate product (VI) which has been postulated has not been isolated in this work. The position of the unsaturation in dicyclohexenylsulfone, cyclohexenylsulfinic or sulfonic acid and octahydrodiphenyl has not been fixed. The octahydrodiphenyl which was obtained in this work was not identical with the conjugated diene reported by Wallach.[7]

The end valences in the polymer are apparently satisfied by the addition of the elements of water and apparently there is a hydrocarbon group at each end since the molecule is not an acid as it would have to be if a sulfur dioxide group at one end of the chain added either a hydrogen atom or a hydroxyl group. The presence of one hydroxyl group in the polymer was fixed by treating with chloroacetyl chloride to give a monochloroacetyl derivative. The analysis and molecular weight (about 6000) of the chloroacetyl derivative indicated that the complete formula of the polymer could be best represented by formula XII where *n* has a mean value of 39.



The presence of a hydroxyl group was further substantiated by acetylation. The acetylated polymer is more stable toward heat, drying and discoloration in the air than is the original polymer.

Experimental

Preparation of the Cyclohexene–Sulfur Dioxide Addition Compound.—The method finally adopted for the preparation of the polymeric sulfone from cyclohexene was as follows. A solution of 20 cc. of cyclohexene, 5 cc. of 95% ethyl alcohol, and 3 cc. of 2% aqueous hydrogen peroxide in 20 cc. of liquid sulfur dioxide was placed in a tightly stoppered heavy-walled flask and allowed to stand at room temperature (25–30°) for about twenty-four hours. The flask was then cooled in a bath held at about −20°, and opened. The viscous mass remaining in the flask was dissolved in 50 cc. of chloroform. The polymer was then precipitated by adding a large volume (300 cc.) of ether to this solution. The polymer was collected on a Buchner funnel and sucked dry. After the solvent was removed, the solid was powdered in a mortar, washed thoroughly with ether, and again collected in a suction filter. The yield was 27–29 g. (93–100% of the theoretical amount). The product turned brown when dried at 76° in an Abderhalden drier. The products prepared varied in composition, but fell in the following limits.

Anal. Calcd. for $(C_6H_{10}SO_2)_{40}C_6H_{11}OH$: C, 49.4; H, 6.98; S, 21.9. Found: C, 45.1 to 47.1; H, 6.3 to 6.73; S, 21.46 to 21.56.

It will be noted that these carbon and hydrogen analyses run low. The same is true for others reported in this paper. It was thought that some oxidation might be taking place and that the darkening of the polymer was due to oxidation. However, samples which had become quite brown gave the same analyses as did the freshly prepared white polymer.

Before finally arriving at the above method of preparation a great many other procedures were studied. The addition product was first prepared by treating liquid sulfur dioxide with cyclohexene prepared by the dehydration of cyclohexanol.[8] The yields were variable. Some cyclohexene was treated with ethylmagnesium bromide to remove various possible oxygen-containing materials and then distilled. This purified cyclohexene did not combine with sulfur dioxide. Traces of alcohols and aldehydes added to the cyclohexene would catalyze the addition reaction but the yields were still erratic. Partially ozonized cyclohexene and benzoyl peroxide were added to the reaction mixture, but they had no marked effect. Neither ultraviolet light nor sunlight would catalyze the reaction.

The use of 2% aqueous hydrogen peroxide gave satisfactory and consistent results in every trial. The product obtained from the different reaction mixtures which gave an addition compound seemed to be the same substance or mixture of substances. If the alcohol was not present in the reaction mixture the addition compound usually darkened on exposure to the air. About a dozen common alcohols were used in different reaction mixtures. There seemed to be no difference in the products obtained in these runs, yet all products were whiter than could be obtained when no hydroxyl compound was present. The presence of a small amount of antioxidant such as hydroquinone or pyrogallol in the reaction mixture completely inhibited the formation of the addition product.

A product apparently identical with the compound described here was obtained by bubbling sulfur dioxide and oxygen through cold cyclohexene. This procedure was less satisfactory than the pressure bottle method for producing white polymer.

Physical Properties of the Polymer.—The addition product was a white, amorphous solid which was very hard and brittle. It did not melt sharply but softened and decomposed at slightly above 200°. It was quite soluble in chloroform and tetrachloroethane and somewhat soluble (4–5%) in dioxane and nitrobenzene. It was insoluble in other common organic solvents. Evaporation of a dilute chloroform solution of the polymer left a brittle film. The polymer was insoluble in water, dilute acids, and dilute alkalies. It dissolved slowly in concentrated sulfuric acid and was precipitated apparently unchanged when this solution was poured into water.

Cryoscopic molecular weight determinations in dioxane and nitrobenzene gave very unsatisfactory results, and the molecular weight of a given sample varied from 660 to 1840 in different trials in the same solvent. The polymer

---

[7] Wallach, *Ann.*, **381**, 112 (1911).

[8] "Organic Syntheses," Coll. Vol. I, p. 177.

was insoluble in camphor and the Rast micro method[9] could not be used for molecular weight determination.

Search for the End Groups in the Polymer.—Samples of the resin prepared in the presence of ethylene chlorohydrin or *p*-bromobenzyl alcohol in place of the usual ethyl alcohol, did not contain halogen. Substitution of *m*-bromobenzaldehyde for the paraldehyde as a catalyst in the preparation of the polymer did not give a product containing halogen. The polymer did not liberate a measurable amount of gas when treated with propylmagnesium bromide in dibutyl ether solution. The presence of a hydroxyl group was established by acylation.

Acetyl Derivative.—Ten grams of the polymeric sulfone prepared in the usual manner was dissolved in 40 cc. of acetyl chloride in the cold. A water white solution was obtained. The viscous solution was poured very slowly into a large volume (3 liters) of ice water. The solid precipitate was dried on a suction filter, washed thoroughly with water and then with alcohol and ether. The solid was powdered and the washing repeated. The yield was 9.5 g. This product had about the same solubility characteristics as the original polymer. It melted to a clear glass at 210–215°. It did not discolor on standing or heating. Cryoscopic molecular weights in dioxane gave satisfactory results.

Anal. Calcd. for $(C_6H_{10}SO_2)_{40}C_6H_{10}OCOCH_3$: C, 51.4; H, 6.95; S, 21.4; mol. wt., 5981. Found: C, 47.9, 48.0; H, 6.60, 6.13; S, 22.2; mol. wt., 6175, 5960, 5830.

The same white acetyl derivative could be obtained by treating the discolored polymer with acetyl chloride.

Chloroacetyl Derivative.—Ten grams of the polymer was dissolved in 40 cc. of chloroacetyl chloride and treated as described in the preceding experiment. The yield of white solid was 9.5 g., m. p. 215–220°. The precipitated product had the same solubilities as the original polymer. Sodium fusion showed that it contained halogen.

Anal. Calcd. for $(C_6H_{10}SO_2)_{40}C_6H_{10}OCOCH_2Cl$: C, 51.1; H, 6.88; S, 21.2; Cl, 0.58; mol. wt., 6015. Found: C, 47.9, 48.0; H, 6.60, 6.94; S, 21.6; Cl, 0.48, 0.45, 0.45; mol. wt. (cryoscopic in dioxane), 5430.

Treatment of the polymer with α-bromopropionyl chloride also gave a halogen-containing product.

Alkaline Decomposition of the Polymeric Sulfone.—The polymer passed slowly into solution when heated with aqueous alkalies. The concentration of the alkali and the time and temperature of the heating changed the nature of the products which were formed. Cyclohexene was obtained in every case which was studied.

Heating with 17% Sodium Hydroxide.—A mixture of 180 g. of the addition product and 330 g. of approximately 17% of sodium hydroxide solution was heated under a reflux condenser for about fifty hours on the steam-bath. The resin slowly disappeared and a small amount of a gummy solid appeared on the surface of the solution in the flask. After the heating period, a portion of the liquid was distilled off. The distillate separated into two layers. The upper layer (about 10 cc.) was separated and identified as cyclohexene by its boiling point (81–83°) and the melting point of the solid nitrosochloride (149°).[10]

The material which did not distil with water vapor was extracted with ether and the ether solution evaporated. The remaining yellow oil boiled at 185–190° (3 mm.) and gave 5 g. of solid distillate. After recrystallization from petroleum ether this material gave long colorless needles melting at 75°. This solid reduced alkaline potassium permanganate solution, did not decolorize a solution of bromine in carbon tetrachloride, and did not liberate gas on treatment with propylmagnesium bromide in dibutyl ether. Analysis and molecular weight determinations indicate that this product is dicyclohexenyl sulfone.

Anal. Calcd. for $C_{12}H_{18}SO_2$: C, 63.7; H, 8.04; S, 14.1; mol. wt., 226. Found: C, 63.5, 63.6; H, 7.70, 7.89; S, 14.1, 14.2; mol. wt. (Rast), 202, 208.

The ether insoluble material contained sodium sulfite and complex organic sulfur compounds which were not further separated in this experiment.

Decomposition with Hot 90% Potassium Hydroxide.—A mixture of 50 g. of the polymeric sulfone and 35 g. of 90% potassium hydroxide was heated to about 250° in a copper flask equipped with a condenser set for distillation. The distillate separated into two layers, one of which was water. The organic material in the distillate was dried over magnesium sulfate and redistilled. About 7 g. of cyclohexene (b. p. 82–84°) was obtained. The next portion (4 g.) boiled at 234°; n^{20}_{D} 1.5090; d^{20}_{4} 0.9293; M_D for $C_{12}H_{18}$: 52.56. Found: 52.3. *Mol. wt.* Calcd. for $C_{12}H_{18}$: 162. Found (cryoscopic in benzene): 150, 149.5.

This compound combined with bromine in chloroform solution to yield a solid tetrabromide, which after crystallization from alcohol melted at 158°.

Anal. Calcd. for $C_{12}H_{18}Br_4$: Br, 66.35. Found: Br, 66.51.

The hydrocarbon was apparently an octahydrodiphenyl which was isomeric with the one having conjugated double bonds which has been described by Wallach.[7]

Reduction of this hydrocarbon by hydrogen in the presence of a platinum catalyst[11] gave dodecahydrodiphenyl, b. p. 236°; n_D 1.4800; d^{20}_{20} 0.888. The constants reported in the literature[12] are b. p. 233°; n_D 1.4770; d^{20}_{20} 0.873.

The residue in the copper flask contained a large amount of potassium sulfite. There was little or no sulfate ion present. This material was acidified with sulfuric acid and the sulfur dioxide was expelled. The remaining solution was exactly neutralized with sodium carbonate and evaporated to dryness. The residue was extracted with 95% alcohol and this extract was evaporated to dryness. By extracting this residue with absolute alcohol and again evaporating the solution to dryness a gummy residue was obtained. This material was partially soluble in water and on treatment with a little nitric acid and silver nitrate gave an insoluble silver salt which from its analysis seemed to be silver cyclohexenyl sulfinate or sulfonate.

Anal. Calcd. for $C_6H_9SO_2Ag$: S, 12.6. Found: S, 12.2.

---

[9] Rast, *Ber.*, **55**, 1051 3727 (1922).

[10] Baeyer, *Ann.*, **278**, 108 (1893); Wallach, *ibid.*, **343**, 49 (1905). The melting point given in the literature is 152–153°. A mixture of the material described above with an authentic sample of this compound showed no depression in melting point.

[11] Adams and Shriner, "Organic Syntheses," Coll. Vol. 1, p. 452.

[12] Sabatier and Murat, *Compt. rend.*, **154**, 1390 (1912).

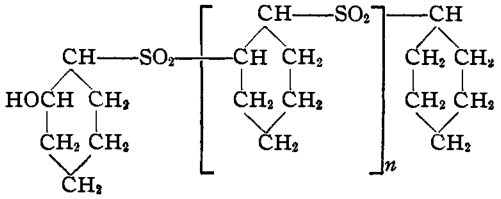
A considerable amount of sulfur containing organic material of the consistency of vaseline remained behind in the various alcohol extractions. Its composition was not determined.

Hydrolysis with 5% Sodium Hydroxide.—A mixture of 50 g. of the polymer and 140 cc. of 5% sodium hydroxide solution was heated under a reflux condenser on a steam-bath for about five days. Very little cyclohexene was produced. This solution was extracted with ether and the ether was evaporated. The residue was recrystallized from alcohol and melted at 138°. It contained sulfur; did not decolorize bromine in carbon tetrachloride solution; was not oxidized by alkaline potassium permanganate solution; and was insoluble in water, dilute acids or dilute alkalies. The analysis and molecular weight indicated that this product was dodecahydrophenoxthine dioxide.

Anal. Calcd. for $C_{12}H_{20}SO_3$: C, 59.02; H, 8.26; S, 13.1; mol. wt., 244. Found: C, 58.99; H, 8.24; S, 13.3; mol. wt. (cryoscopic in benzene), 236, 238.

Summary

1. It has been found that sulfur dioxide adds to cyclohexene in the presence of an oxidizing catalyst to produce a polymeric sulfone whose most probable structure is



2. Treatment of the polycyclohexene sulfone with chloroacetyl chloride yields a product containing halogen. Halogen analyses and molecular weight determinations indicate that the value of "*n*" is about thirty-nine, *i. e.*, the molecular weight is approximately 6000.

3. Isolation of octahydrodiphenyl, dicyclohexenyl sulfone, dodecahydrophenoxthine dioxide, cyclohexene, cyclohexenyl sulfinic or sulfonic acid and potassium sulfite from the alkaline decomposition of the polymer substantiate the above formula.

URBANA, ILLINOIS RECEIVED JUNE 20, 1934

COMMUNICATIONS TO THE EDITOR

IODINE CATIONS

Sir:

Philbrick [THIS JOURNAL, **56,** 1257 (1934)] and Faull and Baeckström [*ibid.*, **54,** 620 (1932)] have recently concluded that the number of iodine cations in a solution of iodine monochloride is negligible. It was demonstrated in 1920 [Howell and Noyes, THIS JOURNAL, **42,** 991 (1920)] that the iodine of a number of acetylene derivatives reacts in the positive form. It is true that we did not then recognize the sharp distinction between covalent and ionic linkages which Sidgwick has shown so conclusively in his Monograph ("Some Physical Properties of the Covalent Link in Chemistry," Cornell University Press, 1933), but the demonstration that iodine may react as a cation is still satisfactory. While very many reactions of chlorine and hypochlorous acid demonstrate the existence of chlorine cations, these cannot be shown by electrometric measurements [Noyes and Wilson, THIS JOURNAL, **44,** 1633 (1922)].

The iodine cation must have the structure, $:\underset{..}{\overset{..}{\mathrm{I}}}.$ It has recently been pointed out [Noyes, *ibid.*, **55,** 658 (1933)] that while six-electron ions frequently take part in reactions the number of such ions is always small. The structure of several hundred thousand carbon compounds has been determined on the fundamental assumption that radicals are transferred from one compound to another in chemical reactions. The results are universally accepted in spite of the fact that only a very few of the radicals have been isolated. Similar methods may be used to advantage in determining the electronic structure of many compounds and radicals. The anion ICl_2^- is assumed in the papers referred to. This is possible only by assuming a coördination number of 5 for iodine, with six unshared electrons, $:\underset{..}{\overset{..}{\mathrm{Cl}}}\;\overset{-}{\underset{..}{\overset{..}{:\mathrm{I}:}}}\;\underset{..}{\overset{..}{\mathrm{Cl}}}:$, making the iodine negative, or that a chloride ion is held to the iodine atom by static attraction because of the positive dipole moment of the iodine monochloride. The latter appears more probable but the choice should be determined by x-ray measurements.

UNIVERSITY OF ILLINOIS WILLIAM A. NOYES
URBANA, ILLINOIS

RECEIVED JUNE 19, 1934