then increases again to *ca.* 0.055 in 12 *M* HCl. $E_{Ni}$ on the other hand was found to be *ca.* 2.5 throughout the whole acid range. The difference in the adsorption behavior of the two elements is sufficient to permit excellent separation. Since as discussed earlier[3] $E = 1/(i + D)$ where $i$ is the fractional interstitial space and $D$ the distribution coefficient (amount per ml. of resin/amount per ml. of solutions), small values of $E$ indicate good adsorption. Furthermore, $E$ will reach a maximum value ($E_{max} = 1/i$) when $D$ becomes zero. Using sodium and potassium tracers and assuming that their ions are not adsorbed $E_{max}$ = *ca.* 2.5 was found for these columns. Hence there is negligible adsorption of nickel in the range 0.5 to 12 *M* HCl and of cobalt in the range 0.5 to 3 *M*.

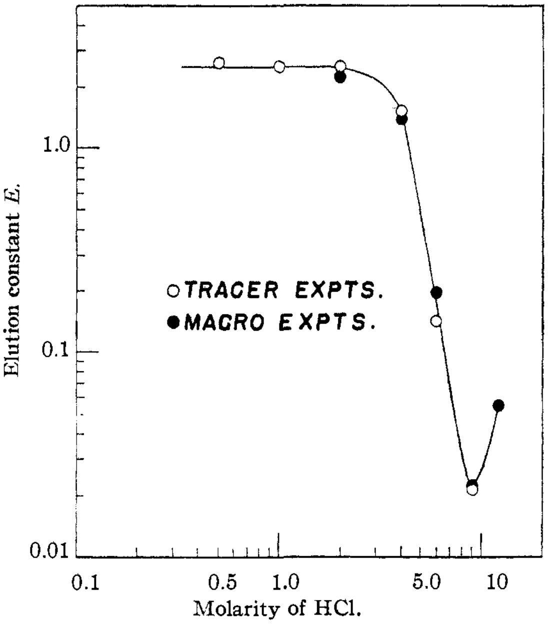

Fig. 1.—Adsorption of cobalt on Dowex-1.

Cobalt is adsorbed as a blue band which is sufficiently intense to permit detection of traces of cobalt (0.5 microgram in 9 *M* HCl was detectable on a 0.023 cm.$^2$ column). Such tests have also been carried out as batch experiments. For example, 1 mg. of Dowex-1 was stirred into 0.5 cc. of 9 *M* HCl containing 4 mg. of reagent grade $NiCl_2 \cdot 6H_2O$ (with 0.13% cobalt). The suspension was slowly dropped onto filter paper. A blue ring of resin (indicating cobalt) formed as the green solution dispersed through the paper.

A comparison of the adsorption data of cobalt with those of iron(III)[4] is of interest. The latter shows very much greater adsorption in concentrated HCl and no maximum as does cobalt near 9 *M* HCl. It had been shown earlier[3] that very strong adsorption in concentrated HCl is probably characteristic of singly negatively charged complex ions and that doubly (or higher) negatively charged complexes in this medium are relatively poorly adsorbed. The adsorbed ion in the case of iron has been identified with $FeCl_4^-$ through resin-capacity measurements,[5] further supporting the earlier conclusions. Additional evidence for the reasonably general applicability of this rule comes from the observation that gallium (probably as $GaCl_4^-$) is adsorbed quantitatively similarly to iron ($FeCl_4^-$).[6] One might thus tentatively assume that $FeCl_4^-$ and $CoCl_3^-$ are also approximately equally strongly adsorbed. On this basis the fraction of cobalt as $CoCl_3^-$ can be estimated to be considerably less than 1% even in 9 *M* HCl, the adsorption maximum.

Since in concentrated HCl a negatively charged complex of cobalt almost certainly exists in considerable concentration[7,8,9] one can conclude that it is not strongly adsorbed. Since this ion probably has a charge of minus two ($CoCl_4^{=}$)[7,8] this relatively poor adsorption in concentrated HCl is in general agreement with the earlier conclusion that in this medium only singly negatively charged complexes are extremely strongly adsorbed.

The non-adsorbability of Ni(II) by the resin suggests very strongly that negatively charged complexes of this element are not formed in appreciable concentration even in concentrated hydrochloric acid.

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(4) G. E. Moore and K. A. Kraus, This Journal, **72**, 5792 (1950).

(5) K. A. Kraus and G. E. Moore, unpublished results.

(6) K. A. Kraus, F. Nelson and G. W. Smith, unpublished results.

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## Ethyl α,α-Dibromo-γ,γ,γ-trifluoroacetoacetate

By William L. Mosby

Although the preparation of ethyl γ,γ,γ-trifluoroacetoacetate was described some time ago,[1] little seems to be known of its α-halogenated derivatives. The preparation and properties of ethyl α-chloro-γ,γ,γ-trifluoroacetoacetate are described by Hill, Towne and Dickey.[2] The bromination of ethyl γ,γ,γ-trifluoroacetoacetate is mentioned by Henne and Mencher,[3] but no details are given.

Ethyl α,α-dibromo-γ,γ,γ-trifluoroacetoacetate has been prepared by the bromination of ethyl γ,γ,γ-trifluoroacetoacetate in the presence of pyridine, using (a) bromine itself, and (b) pyridine perbromide hydrobromide.[4] Both methods gave essentially the same rather low yield of product. In view of the facile chlorination of ethyl γ,γ,γ-trifluoroacetoacetate,[2] perhaps the simpler direct treatment of the ester with bromine would be effective, but as no further work on this compound is contemplated, our data are presented now. The considerable fore-run obtained in the distillations probably represents products formed by cleavage of the ester. Ethyl α,α-dibromo-γ,γ,γ-trifluoroacetoacetate is a colorless, mobile liquid, with a slight, but not unpleasant, odor (in contrast to

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(1) F. Swarts, *Bull. Sci. Acad. Roy. Belg.*, [5] **12**, 679 (1950).

(2) H. M. Hill, E. B. Towne and J. B. Dickey, This Journal, **72**, 3289 (1950).

(3) A. L. Henne and L. Mencher, Abstracts of Papers, 118th Meeting A. C. S., Chicago, Ill., Sept. 3-8, 1950, p. 10L.

(4) C. Djerassi and C. R. Scholz, This Journal, **70**, 417 (1948).

ethyl α-chloro-γ,γ,γ-trifluoroacetoacetate).[2] As would be expected, it fails to form a chelate compound with copper salts.

In an all-glass apparatus, protected from moisture by a calcium chloride tube, a solution of 45 g. (0.245 *M*) of ethyl γ,γ,γ-trifluoroacetoacetate in 100 ml. of dry chloroform was stirred and cooled to about −78° in a Dry Ice–acetone-bath. A solution of 45 g. (0.570 *M*) of dry pyridine and 78.5 g. (0.490 *M*) of dry bromine in 200 ml. of dry chloroform was added dropwise. When all of the bromine solution had been added, the reaction was allowed gradually to warm to room temperature, with gentle stirring for 12 hours, then stirred four hours at 55–60°. The bulk of the chloroform was removed *in vacuo*, and the orange residue warmed and stirred with 400 ml. of dry petroleum ether (b.p. 20–40°). The mixture was filtered, the crystals washed well with more petroleum ether, and the filtrate stripped of solvent *in vacuo*. Vacuum distillation of the residue gave 49.7 g. of orange liquid, b.p. 37–81° (9 mm.). This was redistilled through a small Widmer column from a trace of zinc dust, giving 28.3 g. (34%) of ethyl α,α-dibromo-γ,γ,γ-trifluoroacetoacetate, b.p. 74–5° (9 mm.), $n^{26}$D 1.4420.

*Anal.* Calcd. for $C_6H_5O_3F_3Br_2$: C, 21.03; H, 1.45; F, 16.67; Br, 46.8. Found: C, 21.04; H, 1.46; F, 14.44; Br, 47.4.

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## The Dipole Moment of Ethylgermanium Trichloride

BY ROBERT C. OSTHOFF[1] AND EUGENE G. ROCHOW

Ten years ago Smyth[2] determined the dipole moments of some trialkylgermanium halides, but the dipole moment of ethylgermanium trichloride was not included. Since ethyl- and diethylgermanium chlorides may now be prepared quite readily and conveniently by the direct synthesis,[3] the authors have determined the electric moment of ethyl germanium trichloride and have further characterized this material.

### Experimental

**Ethylgermanium Trichloride.**—Ethylgermanium trichloride was prepared by the direct reaction of ethyl chloride with mixed copper and germanium powders at 317° in the manner that has previously been described.[4] The desired compound was isolated from the reaction mixture by fractional distillation. The fraction boiling at 140.0° and 763 mm. was collected as ethylgermanium trichloride.

The purity of the ethylgermanium trichloride was established by cryoscopic measurement of its molecular weight in anhydrous benzene and by the determination of the molar refraction of the compound. In a typical experiment, a 0.57% solution in benzene showed a depression of the freezing point corresponding to a molecular weight of 202 (calcd., 207.9). At 25.0° the refractive index of the pure ethylgermanium trichloride was found to be 1.4719. By employment of a dilatometric pycnometer the density of this liquid was found to be 1.5953 g./cm.³ at 25.0°. These physical constants lead to a value of the molar refraction, $R^{25}$D, of 36.50 cm.³. If the bond refraction of the Ge–C bond is assumed to be 4.13 cm.³ and the bond refraction of the Ge–Cl bond is taken as 7.89 cm.³, these values in combination with the bond refractivities of Denbigh[5] lead to a calculated molar refraction of 36.1 cm.³.

**Benzene.**—Merck and Co., Inc., Reagent Grade benzene was further purified by drying over phosphorus pentoxide for several weeks. The anhydrous benzene then was fractionated, and the portion boiling at 80.1° at 765 mm. was collected; $n^{25}$D 1.49825 (previously published value, $n^{25}$D 1.49821[6]).

**Dipole Moment.**—Dielectric constants of dilute solutions in benzene were measured with a modified heterodyne–beat apparatus which was similar to that which has been described by Stranathan.[7] By employment of the method of calculation which has been described by Smyth[8], the dipole moment of ethylgermanium trichloride was evaluated. In the calculation of the electric moment the dielectric constant of benzene was taken as 2.273[9] at 25.0°.

In Table I are presented the observed data which were used in the calculation of the dipole moment.

TABLE I

| Mole fraction of solute $c_2$ | Density *d*, g./cm.³ | Dielectric constant *E* | Total molar orientation polarization $P_2$, cm.³ |
|---|---|---|---|
| 0.011649 | 0.88386 | 2.422 | 217.83 |
| .007887 | .87959 | 2.373 | 217.44 |
| .004905 | .87615 | 2.328 | 196.98 |
| .002150 | .87332 | 2.294 | 169.11 |

$P_{2\infty} = 145.0$

In this table $P_{2\infty}$ represents the total molar orientation at infinite dilution (obtained by graphical extrapolation). If the sum of the electronic and atomic polarizations is taken as 1.05 $R^{25}$D, *i.e.*, 38.35 cm.³, the dipole moment of ethylgermanium trichloride is calculated to be 2.28 ± 0.09 *D*. This value is about 10% higher than those of most alkyl chlorides, and compares with 2.06 *D* for 1,1-dichloropropane and 2.028 for *n*-propyl chloride.[10] No value for 1,1,1-trichloropropane is available.[10]

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## Preparation and Polymerization of Aryl Methacrylates and N-Arylmethacrylamides

BY S. PATAI, M. BENTOV AND M. E. REICHMANN

In contradistinction with aliphatic esters and amides of methacrylic acid and with aralkyl methacrylates,[1] only very few aryl methacrylates and N-arylmethacrylamides have been described.[2]

In the framework of a larger investigation, the preparation of the polymers of aryl methacrylates and of N-arylmethacrylamides was desired. The normal method of transesterification of methyl methacrylate failed, when applied to the preparation of the aryl methacrylates; good results were achieved, when methacrylyl chloride was treated with the appropriate sodium phenoxides. In the

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