(3) of a change in slope S of a plot of $\log D$ *vs.* $\log m_{\text{Cit}}$, particularly for Ca(II) and Sr(II). Although the data are too sketchy to permit quantitative conclusions regarding the stability of the species in solution, it can readily be shown that the small values of S are consistent with the assumption that a monocitrate complex (MCit^-) exists for Ra(II), Ba(II), Sr(II), Ca(II) and Mg(II) at low citrate concentrations, and that Be(II) probably exists as a citrate complex with charge −4.

If we designate the adsorbable complex ion as X^{-x} and the eluting anion as A^{-a} and assume that the species X^{-x} is a predominant species, then the equilibrium expression

$$\frac{K}{G} = \frac{(X^{-x})_r^a\,(A^{-a})^x}{(X^{-x})^a\,(A^{-a})_r^x} \qquad (5)$$

can be written for the ion-exchange equilibrium

$$aX^{-x} + x(A^{-a})_r \rightleftarrows a(X^{-x})_r + xA^{-a} \qquad (6)$$

where K is the exchange constant, G the appropriate activity coefficient ratio and where parentheses indicate concentrations of species. Under the assumption that G is constant and that $(A^{-a})_r$ is constant (*i.e.*, that $(X^{-x})_r$ is small compared with $(A^{-a})_r$) equation 5 can be written in the form

$$\text{Const.} = \frac{K}{G}\,(A^{-a})_r^x = D^a\,(A^{-a})^x \qquad (7)$$

since

$$D = \frac{(X^{-x})_r}{(X^{-x})} \qquad (8)$$

By differentiation of equation 7, the equation

$$\frac{\text{d} \log D}{\text{d} \log (A^{-a})} = S = -\frac{x}{a} \qquad (9)$$

is obtained, which implies that the slope S of a plot of $\log D$ *vs.* $\log (A^{-a})$ yields the ratio of the absolute magnitude of the charge of the complex ion to that of the eluting anion.

The eluting anion in the citrate experiments was essentially $\text{Cit}^{\equiv}$, *i.e.*, $a = 3$, and hence S should be $-{}^1/_3$ for a complex ion of charge minus one and $-{}^4/_3$ for a complex ion of charge −4. The experimental value of S for Be(II) is very close to $-{}^4/_3$, permitting the conclusion that its citrate complex probably carries a charge of −4 although, of course, possible non-constancy of G introduces some doubt. These experiments do not permit a decision if the formula of this complex is Be(Cit)_2^{-4} or a basic complex of Be(II) (probably polymeric) of the same negative charge. Such polymeric basic complexes, though not of this charge, have been suggested earlier.[4b]

For the other alkaline earths a slope of $-{}^1/_3$ seems to be approached at low m_{Cit}, as indicated in Fig. 1, and hence these data are consistent with the earlier observation[3] that they form monocitrate complexes MCit^-. In the general vicinity of 0.1 M $\text{Cit}^{\equiv}$, Ca(II) and Sr(II) in particular show an increase in slope (more negative), which would suggest that they, and possibly Mg(II), Ba(II) and Ra(II) as well, tend to form dicitrate complexes ($M\,(\text{Cit})_2^{-4}$).

From the point of view of separations, it is interesting to note that in the range of m_{Cit} studied here the differences in adsorbability of the alkaline earths (except Be(II)) are primarily due to differences in the selectivity of the complexes MCit^- which follow the order $\text{MgCit}^- > \text{CaCit}^- > \text{SrCit}^- > \text{BaCit}^- > \text{RaCit}^-$. The same order of selectivities appears to exist for the complexes M(Cit)_2^{-4}. At very low m_{Cit}, not reached in the experiments reported here, additional differences in adsorbability are expected when the alkaline earth citrate complexes are only formed to a small extent. Since the stability constants of the complexes MCit^- decrease in the same order as the selectivity of these complexes, the differences in adsorption should become greater at very low citrate concentrations, and hence one might expect improved separations under these conditions.

Acknowledgment.—The authors are greatly indebted to Mrs. L. W. Magnusson, Jr., for valuable technical assistance.

OAK RIDGE, TENNESSEE

NOTES

The Barrier Hindering Internal Rotation in Pentafluorochloroethane[1]

By J. G. Aston and T. P. Zolki

Received September 3, 1954

We have recently computed the entropy of the ideal gas at 1 atm. and the normal boiling point of pentafluorochloroethane from measurements of the heat capacity down to 11°K., heats of transition, fusion, vaporization and vapor pressure. The results are summarized in Table I. The quantities tabulated were determined in our calorimeter C by methods and with accuracy discussed before.[2]

The normal modes of vibration of this compound have been derived completely from Raman and infrared data by Nielsen, Liang, Smith and Smith,[3] who assumed accidental degeneracy of the two modes of lowest frequency. These values have been used directly to calculate the vibrational entropy at the normal boiling point. To compute the rotational entropy values of 1.184×10^{-112} g.^{3} cm.^{6} and 6.989×10^{-39} g. cm.^{2}, respectively,

---

[1] Carried out under Contract N6onr-269 T.O. III of the Office of Naval Research. We wish to thank the du Pont Company (Organic Chemicals Dept.) for supplying us with the pure sample and for financial support for the determination of the heat capacities of the liquid.

[2] J. G. Aston, S. V. R. Mastrangelo and G. W. Moessen, This Journal, **72**, 5287 (1950).

[3] J. Rud Nielsen, C. Y. Liang, R. M. Smith and D. C. Smith, *J. Chem. Phys.*, **21**, 383 (1953).

TABLE I

ENTROPY OF C_2F_5Cl FROM THERMAL DATA
(0° C. = 273.16° K.)

0–15°K., Debye function, $\theta = 75.7$, six degrees of freedom	1.91 ± 0.02
15–80.24°K.	17.59 ± .03
Transition, 627.59/80.24	7.82 ± .02
80.24–173.72°K.	19.65 ± .04
Fusion, 448.9/173.72	2.58 ± .01
173.72 to 234.04°K.	9.73 ± .01
Entropy of liquid at 234.04° K.	59.28 ± .13
Vaporization, 4639/234.04	19.82 ± .04
Entropy, real gas, 234.04°K., 1 atm.	79.10 ± .17
$S_{\text{ideal}} - S_{\text{real}}$[a]	0.18 ± .03
Entropy, ideal gas, 234.04°K., 1 atm.	79.28 ± .20

[a] $S_{\text{ideal}} - S_{\text{real}} = \frac{27}{32} R \frac{(T_c)^3}{T} \frac{P}{P_c}$ with $T_c = 351$°K., $P_c = 31.7$ atm.

were computed for the product of principal moments and for the reduced moment assuming tetrahedral angles and the usual bond lengths. The tables of Pitzer and Gwinn[4] were used to compute the barrier hindering internal rotation to bring the "spectroscopic" entropy into agreement with the calorimetric entropy.

The computation of the "spectroscopic" entropy is summarized in Table II which is self explanatory and leads to a barrier of 5300 cal. mole^{-1}. This is about what is to be expected from the barriers in ethane, ethyl chloride and hexafluoroethane.

TABLE II

ENTROPY OF PENTAFLUOROCHLOROETHANE FROM MOLECULAR DATA AT 234.04°K. IN E.U.

S (translation)	39.809
S (vibration)	8.160
S (external rotation)	27.837
	75.81
S int. rot. CF_3, $V = 5300$	3.47
Sum	79.28
Obsd.	79.28 ± 0.20

---

[4] K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 426 (1942).

DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE UNIVERSITY
STATE COLLEGE, PA.
CHEMISTRY DEPARTMENT
MCNEESE STATE COLLEGE,
LAKE CHARLES, LA.

The Effect of Base on the Ultraviolet Absorption Spectra of Phenylacetic Acids

BY ROBERT E. BUCKLES AND KEITH G. BREMER

RECEIVED AUGUST 2, 1954

The base-catalyzed condensation of benzaldehyde with phenylacetic acid in acetic anhydride has been pictured[1] as an aldol-type condensation involving as an intermediate the enolate ion of the mixed anhydride of phenylacetic acid and acetic acid. The present investigation is concerned with a comparison of the change in spectra of *o*-nitrophenylacetic acid, *p*-nitrophenylacetic acid and phenylacetic acid in acetic anhydride and in 95% ethyl alcohol when an excess of the typical basic condensation catalyst triethylamine was added. In acetic anhydride the mixed anhydrides and their corresponding enolate ions would be expected to be the main absorbing species under neutral and basic conditions, respectively, and in 95% ethyl alcohol the corresponding species would be the carboxylic acids and their carboxylate ions. Of the two types of ionic species only the enolate ions would have effective conjugation of the negatively charged center with the aromatic ring, and such conjugation should enhance the absorption spectrum—especially with a nitro group in the *o*- or *p*-position.

This type of result has been observed to some extent. The most pronounced shift in the presence of the base in acetic anhydride was observed for *o*-nitrophenylacetic acid. A comparison of this shift with that observed for the formation of *o*-nitrophenylacetate ion in 95% ethyl alcohol is shown in Fig. 1. The corresponding shifts in acetic anhydride were also somewhat more pronounced than those in 95% ethyl alcohol for *p*-nitrophenylacetic acid and for phenylacetic acid, but the excessive absorption of acetic anhydride below 290 mμ limited the comparison in this solvent to a small part of the spectrum where no peaks were observed.

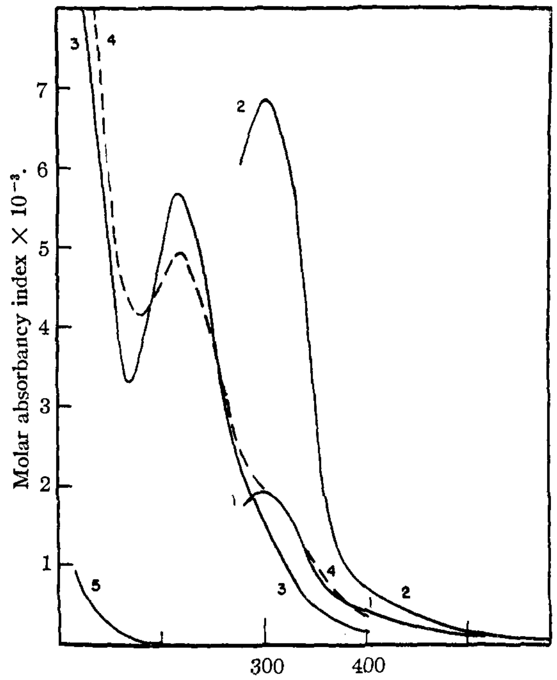

Fig. 1.—Absorption spectra of *o*-nitrophenylacetic acid, (1) 1.00×10^{-4} *M* in acetic anhydride, (2) 1.00×10^{-4} *M* in acetic anhydride containing 2.3×10^{-2} *M* triethylamine (corrected for excess triethylamine), (3) 1.07×10^{-4} *M* in 95% ethyl alcohol, (4) 1.07×10^{-4} *M* in 95% ethyl alcohol containing 3.9×10^{-3} *M* triethylamine (corrected for excess triethylamine), and of (5) 3.9×10^{-3} *M* triethylamine. Triethylamine had negligible values for the molar absorbancy index (molar extinction coefficient) in acetic anhydride above 290 mμ.

---

[1] R. E. Buckles and K. G. Bremer, THIS JOURNAL, **75**, 1487 (1953).