one of the set P$\bar{6}$2c, P$6_3$mc and P$6_3$/mmc requiring the glide plane vanishings {*hh.l*} for *l* odd. No such reflections were observed, but a total of only 21 forms of all types could be recorded. However, a threefold axis (and additional symmetry) will be required of the molecule in any case.

Rigorous application of space group theory requires every atom to have a single equilibrium position; assuming further only that discrete molecules of the assigned composition exist in the crystals we arrive at the following conclusions. No discrete molecule having just four atoms of one kind, *e.g.*, 4Cl in $C_4Cl_4F_4$ or $C_8Cl_4F_8$, can have the symmetry of m3m or 43. Further, no molecule $C_4Cl_4F_4$ or $C_8Cl_4F_8$ of chemically reasonable nature can meet the requirements of $\bar{4}$3m; in particular, neither a cyclobutane nor a tricycloöctane framework, however distorted, can do so. Nor does it seem possible to devise a configuration with threefold symmetry which is also chemically plausible for a molecule $C_6F_{10}$. Certainly the bicyclohexane framework cannot have a threefold axis.

We conclude that for all three substances the molecules in the crystal must have sufficient rotational mobility to give the observed diffraction symmetries as statistical averages over groups of cells containing molecules in various orientations. Previously cited data on the Bragg intensities, the diffuse background scattering, and the physical properties of the crystals support this conclusion. However, the "molecular rotation" cannot be unhindered as is shown by direct experimental evidence of the following sort. Were the rotation entirely "free" the effective electron density in the molecule would be independent of angular variables, *i.e.*, be spherically symmetric, and the reflection intensity would be determined by the value of the quadratic form. But, for example, in $C_8Cl_4F_8$ (333) has several times the intensity of (511), and (551) is far more intense than (711). A slightly different analysis applies to the several possibilities for placing two molecules of $C_6F_{10}$ within the hexagonal unit. Unrestricted rotation of the molecule about the threefold axis (cylindrically symmetric electron density) would in every case require a characteristic extinction of certain reflections which are experimentally recorded. The existence of a restricting potential of appropriate symmetry can scarcely be doubted; the strong coupling of rotation with lattice vibrations is indicated.

We have not attempted to calculate Bragg intensities from an assumed model. Except possibly for $C_4Cl_4F_4$, our lack of definite knowledge of the equilibrium molecular configurations makes the problem a poor choice for study of molecular rotation; and, in contrast with the diffuse background, the Bragg intensities are not sufficiently sensitive to details of the model to promise a strong case for a particular assumed configuration. The simplest case of $C_4Cl_4F_4$ is probably quite complex. Assuming that we have the stable isomer and that the cyclobutane ring is markedly puckered as in $C_4Cl_8$[6] and $C_4F_8$[7] to give a molecule of symmetry $D_{2d}$, there are two alternative configurations to be considered. The four chlorine and the four fluorine atoms give two bisphenoids having a common center, the one elongated the other flattened along the unique axis. Probably there are two not very different minima in the molecular energy corresponding to the assignment of chlorine atoms to one or the other bisphenoid. The packing shapes of the two configurations, as formulated by analogy with $C_4Cl_8$ and $C_4F_8$, are quite different. Either gives easy packing relations within the unit cube for many but not for random orientations of adjacent molecules. Perhaps inversion of molecular configuration between the two extremes plays an important role in the mechanism of "rotation" in the crystal; a further study utilizing data from the purified isomer might be quite profitable.

Based upon the formulas with condensed rings for $C_6F_{10}$ and $C_8Cl_4F_8$, packing models having an assumed angle of folding of 120° between rings sharing an edge (with or without puckering of the individual rings) appear to give packing relations within the respective cells much like the case of $C_4Cl_4F_4$; certain molecular orientations give easy packing relations, but reorientation must involve a coöperative mechanism. We may conclude that the bond diagrams suggested by the methods of synthesis are not inherently improbable in terms of our structural data.

We wish to thank the Atomic Energy Commission for support of this work under Contract No. AT(30-1)-878 with Cornell University.

BAKER LABORATORY OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK

---

[6] T. B. Owen and J. L. Hoard, *Acta Cryst.*, **4**, 172 (1951).

[7] H. F. Lemaire and R. L. Livingston, THIS JOURNAL, **74**, 5732 1952).

---

# Studies in Low Concentration Chemistry. VIII. Some Properties of Tracer Yttrium, Antimony and Silver in Solution

BY GEORGE K. SCHWEITZER AND W. MORRISON JACKSON

RECEIVED JANUARY 8, 1954

The purpose of these experiments was to investigate the radiocolloidal properties of several ions in very low concentration solutions. Yttrium-90, antimony-125 and silver-111 were used as tracers.

## Experimental

**Solutions.**—Solutions of yttrium-90 0.01 *N* in hydrochloric acid and silver-111 0.01 *N* in nitric acid were prepared by previously reported methods.[1] A solution of antimony-125 0.01 *N* in hydrochloric acid was prepared by dilution of a stock solution obtained from the Oak Ridge National Laboratory. The concentrations of the yttrium and silver solutions were established as below $10^{-8}$ *M* and about $10^{-8}$ *M* by spectrographic analysis,[2] and the concentration of the antimony was established at about $10^{-7}$ *M* by a microchemical test by Feigl.[3]

**Techniques.**—Adjustments of *p*H, sample preparations, radioactivity measurements, as well as filtration, centrifugation and adsorption techniques have been described in a previous paper.[4] The main difference in procedure is that

---

[1] G. K. Schweitzer, B. R. Stein and W. M. Jackson, THIS JOURNAL, **75**, 793 (1953); G. K. Schweitzer and J. W. Nehls, *ibid.*, **74**, 6186 (1952).

[2] Private communications from J. H. Gillette, Oak Ridge National Laboratory, and T. DeVries, Purdue University.

[3] F. Feigl, "Laboratory Manual of Spot Tests," Academic Press, Inc., New York, N. Y., 1943.

[4] G. K. Schweitzer and W. N. Bishop, THIS JOURNAL, **75**, 6330 (1953).

nitric acid was used for the adjustment of *p*H with the silver solutions.

**Purification.**—Acidic tracer yttrium solutions were centrifuged, filtered through ultrafine Misco Metallic Filters, or filtered through ultrafine Selas Bacteriological Filters in an attempt to remove suspended impurities. All these experiments were performed in a dust-free atmosphere and all apparatus was washed with centrifuged or filtered water. After centrifugation or filtration, the *p*H values of the solutions were adjusted with centrifuged or filtered sodium hydroxide solution, and then the solutions were centrifuged for 30 minutes. Samples taken from the solutions before this final centrifugation and after centrifugation were counted and used to determine the percentage of yttrium removed.

## Results

Centrifugation of yttrium solutions which had not been purified gave results in agreement with previously reported values using filtration.[5] Up to a *p*H value of 5.0, no yttrium is centrifuged, then the removal increases almost linearly with *p*H up to a *p*H value of 7.0, at which 100% of the yttrium is removed. The percentage removed remains at 100% for higher *p*H values. No differences were noted when the previously purified yttrium solutions were used. Adsorption of tracer yttrium onto Norit A carbon goes from 0% at a *p*H value of 0.0 to 100% at a *p*H value of 5.0, the percentage adsorption then remaining at 100% up to a *p*H value of 12.0. The presence of carbonate had little effect upon the adsorption.

The antimony solutions were filtered and centrifuged at *p*H values from 1.0 to 12.0. From a *p*H value of 1.0 to 8.0 the percentage antimony filtered rose from 15 to 30% then dropped to 20% at a *p*H value of 12.0. The centrifugation curve was almost identical in shape, but was about 10 percentage points lower. Adsorption of antimony on Norit A increased from 60% to a *p*H value of 0.0 to 95% at a *p*H value of 5.0, then dropped to 34% at a *p*H value of 10.0, remaining here up to a *p*H value of 12.0.

Filtration and centrifugation of labeled silver solutions at a *p*H value of 8.0 showed that 55 and 20%, respectively, of the silver was removed at $10^{-6}$ *M* and below and that practically all the silver was separated at $10^{-5}$ *M* and above.

## Conclusions

The use of previously purified yttrium solutions in filtration and centrifugation experiments yielded results similar to those obtained with solutions which had not been purified. Adsorption of tracer yttrium onto Norit A carbon as a function of *p*H differed from the trend shown in centrifugation or filtration. The presence of carbonate does not alter the adsorption behavior to any marked degree, but has a profound influence upon removal by filtration.[1] These observations lead to the conclusion that adsorption of yttrium upon impurities suspended in solution is probably not the major factor involved in the formation of radiocolloids.

Some removal of tracer antimony from its solutions can be realized by centrifugation or filtration, maximum removal occurring in the neutral region. The antimony probably existed partly as a radiocolloid and partly as chloro- or chlorohydroxocomplexes at all *p*H values. Adsorption results showed no similarity to the centrifugation experiments, leading to the conclusion that there is probably no relation.

The results in the silver experiments are what one would expect on the basis of true colloid formation and not for adsorption of silver ions onto suspended impurities.

**Acknowledgment.**—The authors wish to express their gratitude to the U. S. Atomic Energy Commission for Research Grant AT-(40-1)-1058 which supported this work.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TENNESSEE
KNOXVILLE 16, TENNESSEE

---

[5] J. D. Kurbatov and M. H. Kurbatov, *J. Phys. Chem.*, **46**, 441 (1942); G. K. Schweitzer, B. R. Stein and W. M. Jackson, THIS JOURNAL, **75**, 793 (1953).

---

# COMMUNICATIONS TO THE EDITOR

## A NOVEL REARRANGEMENT IN THE SYNTHESIS OF AZULENES

*Sir:*

In the course of work which had as its goal the preparation of 4,7-disubstituted azulenes by a method designed eventually to lead to azulenes derivable from natural sources, 2-methylbicyclo-(5,3,0)-5-decanone (I), b.p. 92–96° (2.5 mm.) (Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.64; H, 11.02); semicarbazone, m.p. 143–143.5° (Calcd. for $C_{12}H_{21}N_3O$: C, 64.54; H, 9.48; N, 18.82. Found: C, 64.58; H, 9.48; N, 19.0) was prepared as follows: Cyclopentanone carboxylic ester was condensed with ethyl $\gamma$-bromo-$\gamma$-methylcrotonate; rearrangement at this stage is excluded by consideration of the infrared spectrum of I (bands at 1705 and 1385 cm.$^{-1}$).[1] The non-enolic character of the condensation product, demonstrated by chemical tests and infrared spectrum, eliminates another, though unlikely, isomerization occurring *via* reversal of the Dieckmann reaction and recyclization in the other direction. Reduction, hydrolysis and decarboxylation furnished an acid whose ethyl ester was condensed with ethyl cyanoacetate. The condensation product was reduced, hydrolyzed and decarboxylated and the resulting dibasic acid cyclized to I through the barium salt.

---

[1] An *S*N2 type rearrangement, would have led to a bicyclo(3,3,0)-octanone derivative possessing a band near 1735–1750 cm.$^{-1}$. A shift from $\alpha,\beta$- to $\beta,\gamma$-type unsaturation in the crotonic ester during bromination, which might have led to a $\delta$-bromo compound, would have resulted in the formation of bicyclo(6,3,0)undecanone and elimination of the C–$CH_3$ band at 1385 cm.$^{-1}$ which appears in all compounds.