

## CarrierFree Radioisotopes from Cyclotron Targets. VIII. Preparation and Isolation of Cu64, 67 from Zinc

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may at high  $N_2O_4$  concentrations be established much more rapidly than the first equilibrium discussed above.

Quantitative study of the three new equilibria reported here provides an excellent approach to the thermodynamic properties of  $ClNO_2$ . For practical reasons the third reaction above is the most suited to accurate measurement, but the studies on all three prove to be self-consistent, employing known thermodynamic properties of the other substances involved. As a result of these studies, a provisional value for the energy of dissociation of  $ClNO_2$  into  $Cl$  and  $NO_2$  of some 32 kilocalories per mole has been found. This figure raises grave doubts regarding the kinetic studies of Schumacher and Sprenger.<sup>1</sup> These authors reported a quasi-unimolecular decomposition of nitryl chloride, this dissociation being considered the rate determining step. However, their measured activation energy was only some 21 kilocalories per mole. It is apparent that the decomposition is vastly more complex than postulated by these authors, and that their studies have no value in discussing theories of quasi-unimolecular reactions.

\* Currently on leave from Stanford University, California.

<sup>1</sup> D. M. Yost and H. Russell, Jr., *Systematic Inorganic Chemistry* (Prentice-Hall, Inc., New York, 1946).

<sup>2</sup> German Patent 509,405 to Karl Dachlauer.

<sup>3</sup> Ogg., Richardson, and Wilson, *J. Chem. Phys.* **18**, 573 (1950).

## Carrier-Free Radioisotopes from Cyclotron Targets.

### VIII. Preparation and Isolation of

#### $Cu^{64,67}$ from Zinc\*

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April 24, 1950

THE radio-copper was produced by bombardment of zinc with 19-Mev deuterons in the 60-in. cyclotron at Crocker Laboratory. At this energy, the longer-lived radioisotopes<sup>1</sup> of copper,  $Cu^{64,67}$ , are produced in a thick target by the nuclear reactions,  $Zn^{64}(d, 2p)Cu^{64}$ ,  $Zn^{66}(d, \alpha)Cu^{64}$ ,  $Zn^{67}(d, 2p)Cu^{67}$ . Radioisotopes of gallium are produced concurrently by the reactions,  $Zn(d, xn)Ga$ . The carrier-free radio-copper was separated from the target element and from the radioisotopes of gallium by a solvent extraction method based on the selective solubility of copper dithizonate in carbon tetrachloride. This procedure,<sup>2</sup> originally developed for the colorimetric determination of microgram quantities of copper, quantitatively extracted  $Cu^{64,67}$  from solutions containing less than approximately  $10^{-8}$  g of copper, the minimum detectable by colorimetry under the experimental conditions used.

A block of spectrographically pure<sup>3,4</sup> zinc was soldered to a water-cooled aluminum target and bombarded for a total of 20  $\mu$ -hr. at an average beam intensity of 10  $\mu$ a. Approximately 1.0 g of the bombarded surface was removed by milling and dissolved in a minimum volume of 12N HCl. The solution was diluted to 5.5N and the gallium activities were extracted with ether after the addition of 10 mg of  $GaCl_3$  carrier. The aqueous phase was evaporated almost to dryness, adjusted to pH 1.0–1.2 with NaOH to a volume of 50 ml and extracted three times with equal volumes of  $CCl_4$  containing 0.001 percent dithizone. Under these conditions, the carrier-free  $Cu^{64,67}$  was quantitatively separated from the target element and from traces of gallium which may not have been completely removed in the previous extraction. The  $CCl_4$  phases were combined, washed twice with 0.1N HCl and evaporated to dryness in a porcelain dish. To remove excess dithizone and to destroy the copper dithizone complex, the dish was heated at 500°C for  $\frac{1}{2}$  hr. The carrier-free  $Cu^{64,67}$  was dissolved in an amount of 0.1N HCl which on neutralization gave an isotonic saline solution of the desired volume for subsequent biological investigation.

The radio-copper was identified by half-life determination, absorption measurement, and by chemical separation with carriers. The decay curve was followed for 500 hr. and showed the 12.8-hr. period<sup>6</sup> of  $Cu^{64}$  and a longer-lived activity which after 100 hr. leveled off into a 72-hr. period. This activity, presumably  $Cu^{67}$ ,<sup>6</sup> was followed for four half-lives and accounted for approximately 3.0 percent of the total beta-activity corrected to the time of bombardment. Absorption measurements 10 hr. after bombardment showed the 0.6-Mev beta-particle and 1.2-Mev gamma-ray reported<sup>6,7</sup> for  $Cu^{64}$ . A tracer amount of activity added to a 1N HCl solution of Ni, Cu, and Ga in carrier amounts was quantitatively recovered in the CuS fraction following precipitation with  $H_2S$ .

We wish to thank Mr. T. Putnam, Mr. B. Rossi, and the 60-in. cyclotron crew at Crocker Laboratory for bombardments and Professor G. T. Seaborg for helpful suggestions.

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† Lieutenant Colonel, U. S. Army, now stationed at Walter Reed Hospital, Washington, D. C.

<sup>1</sup> G. T. Seaborg and I. Perlman, *Rev. Mod. Phys.* **20**, 585 (1948).

<sup>2</sup> E. B. Sandell, *Colorimetric Determination of Traces of Metals* (Interscience Publishers, Inc., New York, 1944).

<sup>3</sup> The zinc was obtained from Johnson Mathey and Company. Copper was not detected by spectrographic analysis.

<sup>4</sup> The reagents and solutions used in the isolation of  $Cu^{64}$  were tested for copper impurity using the method described in reference 2. The water was triple-distilled from glass.

<sup>6</sup> S. N. Van Voorhis, *Phys. Rev.* **50**, 895 (1936).

<sup>6</sup> R. H. Goeckermann and I. Perlman, *Phys. Rev.* **73**, 1127 (1948).

<sup>7</sup> H. Bradt *et al.*, *Helv. Phys. Acta*, **19**, 219 (1946).

## Errata: The Statistical Mechanical Theory of Transport Processes. III. The Coefficients of Shear and Bulk Viscosity of Liquids

[*J. Chem. Phys.* **17**, 988 (1949)]

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EQUATION (6) should read

$$\left[ \frac{(\mathbf{PP})_{AV}}{m} - m\mathbf{uu} \right] \rho^{(1)} = \rho^{(1)} kT \mathbf{1} - \frac{\rho^{(1)} kT}{\zeta} \left[ \dot{\mathbf{e}} - \mathbf{1} \frac{\nabla \cdot \mathbf{u}}{3} \right],$$

where  $\mathbf{1}$  is the unit tensor. The first term  $\rho^{(1)} kT / 3\zeta$  in the second of Eqs. (10) defining bulk viscosity should be omitted. Likewise, the first term  $NmkT / 3v\zeta$  of Eq. (45) should be omitted. In the first line of Eq. (16),  $\nabla \mathbf{P}_1$  should be changed to  $\nabla \mathbf{R}_1$ . In the last line of Eq. (36),  $I(z)$  should read  $I_\alpha(z)$ . In the first line of reference 2, the date should be changed from 1945 to 1943.

The change in Eq. (6) removes kinetic energy transport terms from the bulk viscosity, which in any event, are negligible in liquids, for which the theory is designed. The intermolecular force contribution to bulk viscosity remains unaffected by the change.

The change in Eq. (6) is necessitated by the definition of temperature in the non-equilibrium case

$$\langle \Pi^2 \rangle_{AV} = 3mkT$$

and the retention of  $^{(1)}\mathbf{F}\dagger$ , as yet undetermined by our theory, in Eq. (15), which should read

$$\langle \Pi \Pi \rangle_{AV} - mkT \mathbf{1} = \frac{m}{2\zeta} \left[ \langle \Pi \Pi \rangle_{AV} \cdot \nabla \mathbf{u} + \langle \Pi \cdot \nabla \mathbf{u} \Pi \rangle_{AV} + \mathbf{u} \cdot \nabla \langle \Pi \Pi \rangle_{AV} \right. \\ \left. + \frac{\partial \langle \Pi \Pi \rangle_{AV}}{\partial t} - \langle ^{(1)}\mathbf{F}\dagger \Pi \rangle_{AV} - \langle \Pi ^{(1)}\mathbf{F}\dagger \rangle_{AV} \right] \\ \rho^{(1)} \langle ^{(1)}\mathbf{F}\dagger \Pi \rangle_{AV} = N \int ^{(1)} \mathbf{F}\dagger \Pi f^{(1)} d\mathbf{p}.$$

By taking the trace of both sides of the corrected form of Eq. (15), we obtain

$$\frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T + \frac{2}{3} T \nabla \cdot \mathbf{u} - \frac{2}{3mk} \text{Tr} \langle ^{(1)}\mathbf{F}\dagger \Pi \rangle_{AV} = 0$$

and are led to the corrected form of Eq. (6).

Thus, as in the kinetic theory of gases, there is no momentum transport contribution to the bulk viscosity in view of the non-equilibrium definition of temperature. The intermolecular force term is therefore not only dominant but the only contribution to bulk viscosity.

### Bond Hybridization in the Non-Tetrahedral Carbon Atom. The Heats of Combustion of Spiropentane and Methylcyclobutane

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April 20, 1950

THE method of bond hybridization in non-tetrahedral carbon atoms presented by Kilpatrick and Spitzer<sup>1</sup> has been applied to spiropentane and methylcyclobutane and the values obtained for the bond strengths used to calculate the molal heats of combustion of the gases at 25°C. A comparison of the calculated heats of combustion with those obtained from combustion measurements indicates that the method may be fairly reliable in predicting heats of combustion (formation) of cyclic hydrocarbons.

The calorimeter used for the combustion measurements was of the ordinary (isothermal) type converted from the adiabatic system of Gilbert *et al.*<sup>2</sup> The energy equivalent was determined by combustion of benzoic acid, NBS standard sample 39f, having the certified value  $26,428.4 \pm 2.6$  int. joules per gram mass for the isothermal heat of combustion under standard conditions.<sup>3</sup> The factor, 4.1833 int. joules per cal., was used in converting to calories. The average value of the energy equivalent of the system found from the calibration experiments was 2805.85 cal./deg. with an average deviation of 0.01 percent and a maximum deviation of 0.02 percent.

The materials for combustion were of the highest purity supplied by the U. S. Bureau of Mines, Bartlesville, Oklahoma, and the NACA. For combustion, the liquids were sealed in glass ampoules and benzoic acid was used as kindler when the usual procedure of adding oil produced no satisfactory combustions. The great difficulty in obtaining good combustions of the highly volatile liquids resulted in only three apparently satisfactory (i.e., no evidence of spattering or carbon deposits in the bomb after combustion) determinations for spiropentane and five for methylcyclobutane before the samples were depleted. From these combustions, there was obtained for the heat of combustion in kcal. per mole of liquid at 25°C and 1 atmos. pressure,  $-\Delta H_R = 778.7_2$  for spiropentane, and  $801.1_4$  for methylcyclobutane, the deviation between extremes being 0.04 percent. For comparison with the theory, these values were converted to the molal heats of combustion of the gases by employing Trouton's rule to calculate the heats of vaporization.

The results of the present work, together with data for some other strained cyclic hydrocarbons, are presented in Table I. For obtaining the calculated values, the method and the data for bond strengths given in reference 1 were employed in conjunction with assumed normal<sup>4</sup> C—C and C—H bond energies of 59 and 87 kcal. The orbitals of the central carbon atom in the spiropentane molecule were assumed to remain tetrahedral and their strengths

TABLE I. Comparison of experimental and calculated values of  $-\Delta H_R(\text{gas})$  at 25°C, for some strained cyclic hydrocarbons.

Compound	Structural representation	$-\Delta H_R(\text{gas})$ experimental kcal./mole	$-\Delta H_R(\text{gas})$ calculated kcal./mole
Cyclopropane		504 <sup>a</sup>	503.9
Cyclobutane		648 <sup>a</sup>	647.6
Cyclopentane		793.6 <sup>b</sup>	793.6 <sup>d</sup>
Spiropentane		785.3 <sup>c</sup>	785.6
Methylcyclobutane		807.8 <sup>c</sup>	806.3

<sup>a</sup> G. E. K. Branch and M. Calvin, *Theory of Organic Chemistry* (Prentice-Hall, Inc., New York, 1941). Recently the value 499.9 has been given for cyclopropane by Knowlton and Rossini, *J. Research Nat. Bur. Stand.* **43**, 113 (1949).

<sup>b</sup> Spitzer and Huffman, *J. Am. Chem. Soc.* **69**, 211 (1947).

<sup>c</sup> This work.

<sup>d</sup> Only 1 kcal. for torsional strain has been added to the calculated value because of relief of strain by non-planar configurations of the ring. See Kilpatrick, Pitzer, and Spitzer, *J. Am. Chem. Soc.* **69**, 2483 (1947).

in the directions of the other four carbon atoms ( $\angle \text{C}-\text{C}-\text{C} = 60^\circ$ ) calculated to be 1.862. The calculated values in Table I contain a torsional strain energy of 2 kcal. per opposed  $\text{CH}_2$  group,<sup>5</sup> and the methyl group of methylcyclobutane was regarded as a hydrogen atom in making this correction.

Because of the difficulties accompanying determinations of heats of combustions of highly volatile liquids by use of the bomb calorimeter, there is a possibility that the  $-\Delta H_R$  values given above for spiropentane and methylcyclobutane are more uncertain than we have indicated, and they should, therefore, be regarded as preliminary. However, because of the good agreement of the observed and calculated values for  $-\Delta H_R(\text{gas})$ , we feel that our results should be presented at this time.

We are grateful to Professor E. C. Gilbert for many helpful suggestions, and to the General Research Council of Oregon State College for funds which made possible the alteration of the calorimeter. The generosity of the late Dr. Hugh M. Huffman of the Bartlesville Laboratory, and Addison M. Rothrock, NACA, in supplying samples is especially appreciated.

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<sup>1</sup> J. E. Kilpatrick and R. Spitzer, *J. Chem. Phys.* **14**, 463 (1946).

<sup>2</sup> Hughes, Corruccini, and Gilbert, *J. Am. Chem. Soc.* **61**, 2639 (1939); Davies and Gilbert, *ibid.* **63**, 2730 (1941); for a detailed description of the present calorimeter, combustions, and calculations, see George L. Humphrey, Ph.D. thesis, Oregon State College (1949).

<sup>3</sup> R. S. Jessup, *J. Research Nat. Bur. Stand.* **29**, 247 (1942).

<sup>4</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1942).

<sup>5</sup> K. S. Pitzer, *Science* **101**, 672 (1945).