TABLE I

| Reactant | Isolated or expected product | Yield, % | M.p., °C. | Reported m.p., °C. |
|---|---|---|---|---|
| β-Naphthoic acid | β-Naphthylamine | 82 | 107–109 | 111–112 |
| α-Naphthoic acid | α-Naphthylamine | 80 | 43–45 | 50 |
| Benzoic acid | Aniline hydrochloride | 66 | 190–192 | 198 |
| *m*-Toluic acid | *m*-Toluidine hydrochloride | 76 | 223–225 | 228 |
| *p*-Toluic acid | *p*-Toluidine hydrochloride | 72 | 238–239 | 243 |
| *o*-Bromobenzoic acid | *o*-Bromoaniline hydrochloride | 53[a] | | |
| *m*-Bromobenzoic acid | *m*-Bromoaniline hydrochloride | 46[a] | | |
| *p*-Bromobenzoic acid | *p*-Bromoaniline hydrochloride | 43[a] | | |
| *p*-Chlorobenzoic acid | *p*-Chloroaniline | 32 | 69–70 | 70–71 |
| Salicylic acid | Benzoxazolone | 33[b] | 137–138 | 138 |
| *o*-Phenylbenzoic acid | Phenanthridone | 40 | 292 | 293 |
| *m*-Nitrobenzoic acid | *m*-Nitroaniline | 53 | 109–110 | 112 |
| *o*-Nitrobenzoic acid | *o*-Nitroaniline | 0 | | |
| *p*-Nitrobenzoic acid | *p*-Nitroaniline | 0 | | |
| Valeric acid | *n*-Butylamine | 0 | | |
| Caprylic acid | *n*-Heptylamine | 0 | | |
| Ethyl benzoate | Aniline hydrochloride | 68 | 190–193 | 198 |
| Benzamide | Aniline hydrochloride | 43 | 190–193 | 198 |
| Benzoyl chloride | Aniline hydrochloride | 51 | 189–192 | 198 |
| Benzonitrile | Aniline hydrochloride | 20 | 190–192 | 198 |
| *p*-Chlorobenzamide | *p*-Chloroaniline | 0 | | |
| Benzanilide | Aniline hydrochloride | 76 | 188–191 | 198 |
| *p,p'*-Dichlorobenzanilide | *p*-Chloroaniline | 48 | 66–70 | 70–71 |
| *p,p'*-Dichlorobenzophenone oxime | *p*-Chloroaniline | 40 | 65–68 | 70–71 |
| *p,p'*-Dichlorobenzophenone | *p*-Chloroaniline | 15 | 69–70 | 70–71 |
| Benzophenone | Aniline hydrochloride | 66 | 188–191 | 198 |
| N-Methyl-*p*-chlorobenzamide | *p*-Chloroaniline, methylamine | 0 | | |
| N-Methylbenzamide | Aniline, methylamine | 0 | | |

[a] Identity confirmed by conversion to acetyl derivative. [b] Recrystallized once from water.

it was filtered from the basic solution directly and then dried. The yields of crude amines or amine hydrochlorides obtained in this way are reported in Table I.

**β-Naphthylamine.**—To a mixture of 1.7 g. (0.24 mole) of hydroxylamine hydrochloride and 4.0 g. (0.23 mole) of β-naphthoic acid was added 50 g. of polyphosphoric acid. The mixture was stirred mechanically and the temperature was gradually raised. At 160° the evolution of carbon dioxide had ceased and the brown mixture was poured over 250 g. of crushed ice. Filtration of the resulting mixture yielded 0.7 g. of an orange colored solid, which displayed no definite melting point. The filtrate was neutralized with potassium hydroxide and the precipitated amine was collected and dried. The yield was 2.7 g. (82%) of light tan α-naphthylamine, m.p. 107–109° (lit. 111–112°).

**Aniline from Benzophenone.**—To a mixture of 2.1 g. (0.030 mole) of hydroxylamine hydrochloride dissolved in 20 g. of polyphosphoric acid was added 1.82 g. (0.010 mole) of benzophenone. The mixture was heated with constant stirring to 160–165° for ten minutes. The purple mixture was poured over 100 g. of crushed ice and the small amount of insoluble material was removed by filtration. The filtrate was made strongly basic with potassium hydroxide and then extracted thoroughly with benzene. The extracts were dried over sodium hydroxide and then saturated with dry hydrogen chloride. The precipitated aniline hydrochloride was collected and dried in a desiccator. The dry hydrochloride had a light purple tinge and melted at 188–191°. The yield was 1.72 g. (66%).

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## Predicted Isotopic Enrichment Effects in Some Isotopic Exchange Equilibria Involving Carbon-14

BY D. R. STRANKS AND G. M. HARRIS

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The equilibrium constants of a considerable number of isotopic exchange reactions have been predicted by the methods of statistical thermodynamics.[1,2] No data of this type have been reported in regard to carbon-14/carbon-12 exchanges. Concurrently with a recent experimental study of such an exchange,[3] it was found desirable to make a number of predictions of this nature. This note presents a brief summary of the results of these and of some additional computations, in the belief that they may prove of interest to others investigating carbon-14 isotope effects.

The procedure was as given by Urey,[1] utilizing the spectroscopic data referred to in the tabulation below. The vibrations for the corresponding carbon-14-containing compounds were determined by use of the harmonic oscillator approximation for diatomic molecules,[4] and of normal vibration equations (usually the valence-force-field approximation) for polyatomic molecules.[5] In certain indicated instances, earlier frequency assignments were checked or modified on the basis of the vibration equation treatment. The partition function ratios $Q_{14}/Q_{12}$ at the three temperatures 273.16, 293.16 and 313.16°K., respectively, are given for each of the eighteen compounds treated. The equilibrium constant of any probable exchange reaction between a pair of these compounds at any of the temperatures given is then readily predicted

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[1] H. C. Urey, *J. Chem. Soc.*, 562 (1947).

[2] A. P. Tudge and H. G. Thode, *Can. J. Research*, **B28**, 567 (1950).

[3] D. R. Stranks and G. M. Harris, *J. Phys. Chem.*, **56**, 906 (1952).

[4] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

[5] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

TABLE OF RESULTS

| Molecule | $Q_{14}/Q_{12}$ 273.16°K. | $Q_{14}/Q_{12}$ 293.16°K. | $Q_{14}/Q_{12}$ 313.16°K. | Spectral data reference[a] | Remarks |
|---|---|---|---|---|---|
| HCHO | 1.574 | 1.515 | 1.467 | 1, p. 300 | |
| $HCO_3^-$ | 1.509 | 1.451 | 1.403 | 2 | Freq. assgt. made on basis of VFF calcn. as $(OH)CO_2$ |
| $CO_3^{=}$ | 1.478 | 1.424 | 1.378 | 1, p. 178 | |
| $CO_2$ | 1.444 | 1.397 | 1.358 | 1, p. 276 | Anharmonicity corrections applied |
| $CO(NH_2)_2$ | 1.418 | 1.372 | 1.333 | 3 | $\nu_6$ estd. by VFF calcn. and analogy to $COCl_2$ |
| $HCO_2^-$ | 1.360 | 1.322 | 1.289 | 4 | $\nu_6$ estd. by VFF calcn. with $k_\Delta$ as for $CH_2O$ |
| COS | 1.355 | 1.317 | 1.286 | 1, p. 174 | |
| $(C_2N_2)^{1/2}$ | 1.322 | 1.289 | 1.261 | 1, p. 294 | |
| $CNO^-$ | 1.315 | 1.283 | 1.255 | 5 | |
| ClCN | 1.299 | 1.269 | 1.244 | 1, p. 174 | |
| $COCl_2$ | 1.295 | 1.263 | 1.237 | 6 | Frequency assgt. checked by VFF calculation |
| $SCN^-$ | 1.292 | 1.262 | 1.237 | 1, p. 174 | |
| BrCN | 1.282 | 1.254 | 1.230 | 1, p. 174 | |
| HCN | 1.281 | 1.256 | 1.233 | 1, p. 280 | Anharmonicity corrections applied |
| ICN | 1.265 | 1.239 | 1.216 | 1, p. 174 | |
| $CS_2$ | 1.255 | 1.227 | 1.204 | 1, p. 173 | |
| CO | 1.216 | 1.196 | 1.179 | 7 | Anharmonicity corrections applied |
| $CN^-$ | 1.192 | 1.174 | 1.159 | 1, p. 195 | |

[a] References: (1) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945. (2) R. Duval, C. Duval and J. Lecomte, *Bull. soc. chim. France*, **5**, 517 (1943). (3) K. W. F. Kohlrausch and A. Pongratz, *Z. physik. Chem.*, **B27**, 176 (1934). (4) J. Lecomte, *et al.*, *Cahiers de Physique*, 17 (1943); *Ann. phys.*, **17**, 5 (1942); *Compt. rend.*, **208**, 1401 (1939). (5) J. Goubeau, *Ber.*, **68**, 912 (1935). (6) C. R. Bailey and J. B. Hale, *Phil. Mag.*, **25**, 98 (1938). (7) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules." D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 522.

by the division of the required pair of partition function ratios.

Reactions involving species of great chemical similarity and which undergo rapid exchange show the expected small enrichment effects. Thus, in the case of the important biological equilibrium

$$HC^{12}O_3^- + C^{14}O_3^{=} \rightleftarrows HC^{14}O_3^- + C^{12}O_3^{=}$$

at 293.16°K., $K = 1.451/1.424 = 1.019$. This represents but a 1.9% enrichment of carbon-14 in the bicarbonate. On the other hand, a number of probable exchanges, so far for the most part uninvestigated experimentally, should exhibit appreciable enrichments. There is the series involving cyanide ion—in addition to the $CN^-$/HCN system (well-known in carbon-13 studies) with a predicted 6.8% effect at 293.16°K., there are those comprising $CN^-$ and $CNO^-$ (9.2%), $CNS^-$ (7.5%), $C_2N_2$ (9.8%), ClCN (8.1%), BrCN (6.8%) and ICN (5.5%). Additional particularly intriguing possibilities are the low-temperature catalytic equilibration (say on active $MnO_2$) of CO and $CO_2$ with a predicted enrichment of no less than 16.8% at 293.16°K., the photochemical exchange of CO with $COCl_2$ (6.5%), the very probable $CO_2$/COS exchange (6.1%), and the significant $CO(NH_2)_2$/$CNO^-$ system (6.9%).

It will be noted that the predicted enrichments for certain of the systems studied here are somewhat greater than twice the values previously given in the literature for the corresponding carbon-13/carbon-12 systems. For example, Urey[1] reports a carbon-13 enrichment of 3.4% for the HCN/$CN^-$ system at 273°K., while the carbon-14 value deduced from our table is 7.5% at the same temperature. Close examination shows that this apparent disagreement with theory stems from the vibrational frequencies used for the isotopic HCN molecules. Our method of calculation (using the VFF equations given by Herzberg[5]) gives for $HC^{13}N$ the frequencies 1969, 723 and 3431 cm.$^{-1}$, respectively, as compared to Urey's values of 1967, 723 and 3435 cm.$^{-1}$.

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## Heats of Hydrolysis of Amide and Peptide Bonds[1]

BY JULIAN M. STURTEVANT

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In recent publications,[2,3] a procedure for the calorimetric determination of the heats of hydrolysis of amide and peptide bonds has been described. The present note reports the application of the method to the hydrolysis of the amide bond of glycyl-L-phenylalanylamide and the peptide bond of carbobenzoxyglycyl-L-leucine.

### Experimental

Glycyl-L-phenylalanylamide acetate, kindly supplied by Dr. J. S. Fruton of Yale University, was hydrolyzed by cathepsin C, also supplied by Dr. Fruton. Cysteine was added as activator. Kjeldahl analysis gave 14.79% nitrogen, as compared with the theoretical value of 14.94%. Carbobenzoxyglycyl-L-leucine, for which the author is indebted to Dr. R. Lumry of the University of Utah, was hydrolyzed by carboxypeptidase, purchased from the Worthington Biochemical Laboratory. Both reactions were carried out in buffered aqueous solution at 25°, and were accompanied by heat evolution which accurately followed in each case a first-order rate law to more than 90% completion. The former reaction was observed in the *p*H range 4.69 to 5.65; in this range no correction[2] for ionization heats is necessary, since the products are practically completely

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(1) This research was aided by a grant from the Rockefeller Foundation. Presented at the Atlantic City Meeting of the American Chemical Society, September, 1952.

(2) A. Dobry and J. M. Sturtevant, *J. Biol. Chem.*, **195**, 141 (1952).

(3) A. Dobry, J. S. Fruton and J. M. Sturtevant, *ibid.*, **195**, 148 (1952).