scribed. The purified acid melted at 179.5–181°.[6] The position of the acetic acid residue in the acenaphthene nucleus was established by conversion to 5-acenaphthylmethylamine by the Curtius reaction[7] and treatment of the amine with nitrous acid to give 5-hydroxymethylacenaphthene.[8] A mixed melting point of this carbinol with that prepared by the lithium aluminum hydride reduction of the known 5-acenaphthoic acid showed no depression.

Experimental[9]

5-Acenaphtheneacetic Acid.—A mixture comprising 92 g. (0.6 mole) of acenaphthene, 28 g. (0.3 mole) of α-chloroacetic acid, 0.5 g. of potassium bromide and 0.2 g. of ferric oxide was heated on a sand-bath under gentle reflux for 24 hours. During this period of heating, the temperature of the melt reached 220°. The resulting dark mass was cooled and extracted exhaustively with warm 10% sodium hydroxide solution. Acidification of the dark alkaline extract precipitated 30 g. of dark and impure acid melting at 135–150°. There was also obtained 68 g. of dark, alkali-insoluble residue. The crude acid was dissolved in 250 ml. of warm alcohol, filtered, and the dark filtrate slowly diluted with water which precipitated a dark oil. The addition of water was continued until crystallization of the acid from the yellow liquor commenced, after which the solution was decanted from the precipitated oil. Further addition of water to the mother liquor yielded a pale yellow crystalline product, m.p. 150–160°. The precipitated oil was redissolved in alcohol and the separation repeated. There was thus obtained 18 g. of acid (28%, based on α-chloroacetic acid), which was further purified by solution in 300 ml. of hot 5% sodium hydroxide solution from which the sodium salt of the acid crystallized on cooling. It was filtered and washed with ice-water. Solution of the salt in warm water and acidification gave 13.5 g. of acid melting at 176–179°. Recrystallization of the sodium salt and final crystallization from dilute alcohol with the addition of decolorizing charcoal gave colorless needles, m.p. 179.5–181°.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.21; H, 5.70. Found: C, 79.24; H, 5.80.

Attempts to purify the crude alkaline extract of the reaction mixture by repeated crystallization and treatment with decolorizing charcoal were less satisfactory.

The amide was obtained as white needles from *n*-propanol, m.p. 236–237°.

Anal. Calcd. for $C_{14}H_{13}NO$: C, 79.58; H, 6.20. Found: C, 79.80; H, 6.53.

The phenacyl ester was obtained as fine white needles from alcohol, m.p. 89–90°.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.96; H, 5.48. Found: C, 80.00; H, 5.60.

The unreacted acenaphthene contained in the alkali insoluble residue was recovered by distillation, collecting the fraction boiling at 265–274°. There was obtained 39 g. (42% of the initial acenaphthene) which crystallized from alcohol as white needles, m.p. 95–96°, and formed a picrate, m.p. 161°.

Degradation of 5-Acenaphtheneacetic Acid.—The crude acid (7.2 g., 0.034 mole), m.p. 176–179°, was mixed with 40 ml. of dry benzene and 6 ml. of thionyl chloride and refluxed for 2 hours, after which the 5-acenaphtheneacetyl chloride was distilled collecting the fraction b.p. 185–195° at 11 mm. The yellow oil soon solidified; yield 4.6 g. (59%).

A mixture comprising 4.5 g. of the acid chloride, 2.2 g. of sodium azide, and 50 ml. of dry benzene was refluxed for 6 hours and then filtered. Concentrated hydrochloric acid, 40 ml., was added to the filtrate and the mixture refluxed for 4 hours, cooled, and the separated amine hydrochloride removed by filtration. There was obtained 2.8 g.—65%—of product which was recrystallized from dilute hydrochloric acid.[7]

Anal. Calcd. for $C_{13}H_{14}ClN$: N, 6.37; Cl, 16.16. Found: N, 6.30; Cl, 16.30.

The benzamide of the amine crystallized from dilute alcohol as fine white needles, m.p. 182–184°.

Anal. Calcd. for $C_{20}H_{17}NO$: C, 83.58; H, 5.97. Found: C, 83.33; H, 6.05.

The benzenesulfonamide crystallized as fine white needles from alcohol, m.p. 148–149°.

Anal. Calcd. for $C_{19}H_{17}NO_2S$: C, 70.56; H, 5.28. Found: C, 70.86; H, 5.33.

5-Hydroxymethylacenaphthene.—A solution of 0.2 g. of 5-acenaphthenemethylamine hydrochloride in 75 ml. of water was treated with 8 drops of 3 *N* hydrochloric acid followed by an excess of sodium nitrite solution. This mixture, on standing overnight at room temperature, deposited a white solid which was removed by filtration, dried and crystallized from benzene. The white needles melted at 156–157° (lit. 153.8–154°).[8] A mixed melting point of the 5-hydroxymethylacenaphthene obtained by the degradation of 5-acenaphtheneacetic acid and a sample prepared as described below by the reduction of the known 5-acenaphthoic acid showed no depression.

5-Acenaphthoic Acid.—This acid was prepared in 57% yield by treating 46 g. (0.2 mole) of 5-bromoacenaphthene in 125 ml. of absolute ether with *n*-butyllithium prepared from 30 g. (0.32 mole) of *n*-butyl chloride and 4.5 g. of lithium wire[10] in 200 ml. of ether. The resulting solution was poured on powdered solid carbon dioxide, allowed to stand one hour, acidified, and the precipitated acid filtered. This product was purified by washing a solution in 5% sodium hydroxide with ether followed by precipitation. There was thus obtained 22.5 g. of acid, m.p. 214–218°. Crystallization from dilute alcohol gave a product, m.p. 220–221°.[11]

5-Hydroxymethylacenaphthene by Reduction of 5-Acenaphthoic Acid.—Finely divided solid 5-acenaphthoic acid (19.8 g., 0.1 mole) was slowly added to a solution of 7.6 g. of lithium aluminum hydride in 600 ml. of dry ether[12] contained in a 2-l. three-neck flask fitted with a stirrer and reflux condenser. After stirring for 1 hour, the mixture was decomposed by the slow addition of 250 ml. of 10% sulfuric acid. The precipitated solid was filtered and extracted with warm 5% sodium hydroxide. There was thus obtained 13.8 g. of the carbinol. An additional 2.6 g. was obtained by evaporating the initial ether filtrate to give 16.4 g. (82%) of carbinol which crystallized from alcohol as fine white needles, m.p. 155–156°.

The acetate, obtained by reaction with acetic anhydride in pyridine, crystallized from hexane, m.p. 60.5–61.5°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.64; H, 6.22. Found: C, 79.9; H, 6.31.

Acknowledgment.—The author takes pleasure in thanking the Research Corporation for a Frederick Gardner Cottrell grant to support this work.

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[6] Anderson and Wade[4] were unable to cyclize this acid to 1-pyracenone. Our attempts to effect this ring closure likewise were unsuccessful.

[7] P. A. S. Smith, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 387.

[8] L. F. Fieser and J. E. Jones, THIS JOURNAL, **64**, 1667 (1942).

[9] All melting points are corrected.

[10] Metalloy Corp., Rand Tower, Minneapolis, Minn.

[11] H. Gilman, W. Langham and F. W. Moore, THIS JOURNAL, **62**, 2332 (1940).

[12] R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 2548 (1947).

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Hydrogen Bonding Ability and Structure of Ethylene Oxides

BY SCOTT SEARLES, MILTON TAMRES AND ELLIS R. LIPPINCOTT

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The very low electron donor ability of substituted ethylene oxides, compared with other cyclic ethers, in hydrogen bonding was reported recently.[1] The

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[1] S. Searles and M. Tamres, THIS JOURNAL, **73**, 3704 (1951).

parent compound, ethylene oxide, was not included in the series reported because its boiling point is below the principal temperature at which spectroscopic and calorimetric measurements were made. The study has now been extended to ethylene oxide by measuring the heat of mixing with chloroform at 3°.

The result, compared with similar data for other ethers, is presented in the table and confirms the effect of ring size on electron donor ability previously deduced for cyclic ethers: 3-membered ring < 6-membered ring < 5-membered ring < 4-membered ring. It is also apparent that the usual electronic effects of substituents are operative in the 3-membered ring.

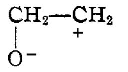
TABLE I

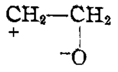
HEATS OF MIXING WITH CHLOROFORM AT 3°

Compound	ΔH (cal./mole)
Ethylene oxide	365
Propylene oxide	470
Epichlorohydrin	185
Styrene oxide	245
Cyclohexane oxide	666
Trimethylene oxide	760[a]
Tetrahydrofuran	750[a]
Tetrahydropyran	640[a]
Diethyl ether	650[a]

[a] From reference 1.

The concept of electron donor ability in hydrogen bonding being a measure of relative electron density[2] leads to the conclusion that the oxygen in 3-membered ring ethers is more positive (or electronegative) than in larger ring ethers or in acylic ethers. This observation may be of interest with regard to the recent proposals for the structure of ethylene oxide. It seems inconsistent with Zimakov's proposal that the structure is a resonance hybrid of I and II with a unit negative charge on each carbon atom,[3] for this would lead to the expectation

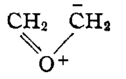

I

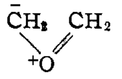

II

that the oxygen would be much less electronegative than usual. Also the C–O dipole would be much greater in ethylene oxide than in acyclic ethers, whereas it actually is about the same.[4-6] Walsh's structures for ethylene oxide and cyclopropane,[7] showing a high electron concentration in the center of the three-membered rings, would suggest that the exterior of such rings would have a lower electron density than normal for the atoms involved. This might explain the poor donor ability of ethylene oxide in hydrogen bonding, but these structural suggestions were not borne out by a recent quantum mechanical analysis.[8] The latter has indicated that, for strained systems, the hybridized orbitals employed for bonding attain maximum overlap in such a way that altered valence angles or "bent bonds" are realized. Detailed calculations were made on cyclopropane, but the results can be applied to other three-membered ring systems.[9]

The orbitals used in these exterior bent bonds of the ring are in a favorable position for some overlap with *p*-orbitals from adjacent atoms, thus giving rise to a conjugation or delocalization effect, which has been observed experimentally with cyclopropyl ketones,[10] α,β-epoxyketones,[7,9] and ethylenimine ketones.[9]

A similar effect can be employed to explain the positive nature of the oxygen atom in ethylene oxide. Since the *p*-orbitals of the oxygen are nominally filled, there can be no overlap of them with the bent bonds of the ring unless the unshared pair of electrons participates in bonding to the carbon atoms. This delocalization, which leads to a formal positive charge on the oxygen, may be expressed by resonance structures III and IV.


III


IV

The fact that the dipole moment of ethylene oxide is smaller and not larger than that of trimethylene oxide[4] is in agreement with these ideas. This delocalization does not cause significant alteration of the normal carbon–oxygen single bond distance,[11] which has been interpreted reasonably on a pure valence state approach (with bent bonds), indicating that III and IV do not make very large contributions. Small changes in electron distribution, however, should make relatively great differences in hydrogen bonding ability and in dipole moments. Such contributions of III and IV may also be partly responsible for the normal carbon–oxygen distance of 1.436 Å. observed in ethylene oxide.[11] Ordinarily one might expect it to be larger because of the weakness of the bond, which is evident from the ease of cleavage by reagents, but any double bond character due to forms III and IV would shorten up the bond.

A similar explanation will apply to other three-membered heterocyclics, the heteroatoms of which formally have unshared but filled p-orbitals. The low basicities observed with ethylenimine and ethylene sulfides (unpublished observations in these laboratories) are in accord.

A delocalization of unshared p-electrons on an atom bonded to a small carbocyclic ring has been postulated by Roberts and collaborators[12] to explain the electronegative character of such rings. In the present case, a delocalization of unshared p-elec-

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(2) M. Tamres, S. Searles, E. M. Leighly and D. W. Mohrman, Abstracts, 122nd Meeting of American Chemical Society, September, 1952, p. 41 M.

(3) P. Zimakov, *Acta Physicochem., U. R. S. S.*, **21**, 401 (1946).

(4) H. D. Robles, *Rec. trav. chim.*, **58**, 111 (1939).

(5) W. L. G. Gent, *Trans. Faraday Soc.*, **45**, 1021 (1949).

(6) There is some difficulty in making a direct comparison, because cyclic ethers normally have considerably higher polarity than their open chain analogs (H. C. Freeman, R. J. W. LeFevre and F. Maramba, *J. Chem. Soc.*, 1649 (1952)). Therefore, comparison with other cyclic ethers with larger rings may be more informative, and here the ethylene oxide dipole does seem abnormally low (ref. 4).

(7) A. D. Walsh, *Nature*, **159**, 712 (1947); *Trans. Faraday Soc.*, **45**, 179 (1949).

(8) C. A. Coulsen and W. E. Moffitt, *Phil. Mag.*, [7] **40**, 1 (1949).

(9) N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952).

(10) M. T. Rogers, THIS JOURNAL, **69**, 2544 (1947); R. P. Mariella and R. R. Raube, *ibid.*, **74**, 518 (1952).

(11) G. L. Cunningham, A. W. Boyd, R. J. Myers, W. D. Gwinn and W. I. LeVan, *J. Chem. Phys.*, **19**, 676 (1951).

(12) M. T. Rogers and J. D. Roberts, THIS JOURNAL, **68**, 843 (1946); J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5031 (1951).

trons on a heteroatom in a three-membered ring is employed to explain the electronegative character of that atom.

Experimental

Heats of Mixing Determinations.—The apparatus and method have been described previously.[13] The ethers were introduced in sealed ampoules in the manner described for volatile ethers in a previous paper.[1] A slightly different value (461 cal./mole) was reported previously for the heat of mixing of propylene oxide with chloroform, but the agreement is within experimental error.

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(13) G. G. Zellhoefer and M. J. Copley, THIS JOURNAL, **60**, 1343 (1938).

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Tracer-diffusion in Liquids. V. Self-diffusion Isoelectric Glycine in Aqueous Glycine Solutions[1]

BY JUI H. WANG

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The ordinary chemical concentration gradient diffusion of isoelectric glycine in its aqueous solutions has been measured by many workers.[2-4] The dependence of these chemical concentration gradient diffusion coefficients upon the concentration of solution have been compared[2] with those calculated from Gordon's formula[5] where D and D_0

$$D = D_0\left(1 + c\frac{\partial \ln y}{\partial c}\right)\frac{\eta}{\eta_0} \qquad (1)$$

are the diffusion coefficients of the solute in its solutions at molal concentration c and at infinite dilution, respectively, y the activity coefficient of the solute at concentration c, and η and η_0 are the macroscopic viscosities of the solution and pure solvent, respectively. Lyons and Thomas showed that for the case of aqueous glycine solutions, the factor (η/η_0) overcorrects the retardation of diffusion due to change in mobility of the glycine molecule. These authors inferred from their measured temperature dependence of the diffusion coefficient of glycine that the above overcorrection is due to the breaking down of the structure of water in the immediate vicinity of glycine molecules.

In self-diffusion, however, since the composition of solution is chemically uniform along the diffusion path, the activity coefficient of the diffusing tracer-molecules is constant, the term $(1 + c \times (\partial \ln y/\partial c))$ reduces to unity. Furthermore, since in self-diffusion there is no net transport of solvent in any direction, the "hydrodynamic effect" of Onsager and Fuoss[6] (which is often referred to as the "electrophoretic effect" in the diffusion of electrolytes) vanishes. We may thus expect the self-diffusion coefficient of isoelectric glycine to be theoretically simpler and hence possibly even more interesting. In the present work the self-diffusion coefficients of isoelectric glycine in its aqueous solutions at 25° are measured and discussed.

Experimental

Tracer Solution.—The radioactive glycine ($^+H_3NCH_2COO^-$) was supplied by Tracerlab, Inc., Boston, Mass., and obtained on allocation from the Isotopes Division, U.S. Atomic Energy Commission, Oak Ridge, Tennessee. The specific activity of this radioactive glycine was about 0.02 mc./mg. A dilute solution of this radioactive glycine in conductivity water was prepared and kept in a sterilized bottle at 0° as stock solution. In making radioactive solution for diffusion measurement, a small measured volume of this stock solution was evaporated to dryness in a platinum crucible under a heat lamp. The radioactive residue (practically invisible) was dissolved in inactive glycine solution of accurately known concentration and with *p*H at 5.98. The increase in total glycine concentration due to the dissolution of the above mentioned radioactive residue is negligible.

Diffusion Measurements.—All the measurements were carried out at 25.00 ± 0.01°. The experimental procedure is the same as that described in Paper I of this series.

Analysis of Samples.—The counting of the radioactive diffusion samples was carried out by means of a windowless flow counter: In order to eliminate errors due to self-absorption of the weak β-particles from C^{14}, the volumes of the c_0-samples were so adjusted that each of them contained approximately the same amount of solid material as the corresponding c_{av}-sample. All samples were dried in desiccators for more than 24 hours before counting. Consequently, the measured values of (c_{av}/c_0), which determine the values of Dt/l^2, are practically free from self-absorption errors.

Results and Discussion

The self-diffusion coefficients of isoelectric glycine in its aqueous solutions at 25° as determined in the present work are listed in Table I.

TABLE I

SELF-DIFFUSION COEFFICIENTS OF ISOELECTRIC GLYCINE IN AQUEOUS GLYCINE SOLUTIONS AT 25°

Concn., mole/l.	$D \times 10^5$, cm.²/sec.
0.01	1.06 ± 0.02
.10	1.05 ± .02
.25	1.03 ± .02
.50	0.990 ± .026
1.00	.929 ± .018
1.50	.871 ± .018
2.00	.830 ± .011

Each value listed in Table I is the average result of 3 to 12 measurements. These self-diffusion coefficients are plotted *vs.* volume molal concentration of glycine in Fig. 1. Diffusion coefficients of glycine for ordinary chemical concentration gradient diffusion as reported by Lyons and Thomas[2] are also included in Fig. 1 for comparison. From the definition of the diffusion coefficients, it is easy for us to see that at infinite dilution the self-diffusion coefficient of isoelectric glycine should be identical to that for chemical concentration gradient diffusion. Figure 1 indicates that as the concentration approaches zero, the two sets of diffusion coefficients tend toward the same limiting value. Since the optical method used by Lyons and Thomas has been developed to a high degree of precision, this agreement can be considered as a further confirmation on the general reliability of the present capillary method for measuring tracer-diffusion in liquids. The dotted curve in Fig. 1 represents values of $D/(1 + c(\partial \ln y/\partial c))$ in equation (1) calculated

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(1) Contribution No. 1135 from the Department of Chemistry of Yale University. Previous papers of this series: THIS JOURNAL, **74**, 1182, 6317 (1952); *ibid.*, 1611 (1952); *ibid.*, 1612 (1952); *ibid.*, **75**, 1769 (1953).

(2) M. Lyons and J. V. Thomas, *ibid.*, **72**, 4506 (1950).

(3) L. G. Longsworth, *ibid.*, **74**, 4155 (1952).

(4) See E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943, p. 412 for earlier references.

(5) A. R. Gordon, *J. Chem. Phys.*, **5**, 522 (1937).

(6) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).