Winkler. In spite of the success of certain conclusions drawn by Ross,[7] based on the hypothesis that the observed discontinuity is due to a first-order transition, the evidence lacked the important further authority that could be provided by results at different temperatures. This communication reports the adsorption isotherms of ethane on sodium chloride crystals at 136.0, 131.3 and 122.9° K. These isotherms confirm the existence of a discontinuity and strongly support its interpretation as a first-order phase transition. Figure 1 shows the three isotherms. The isotherm at 122.9°K., with its marked vertical discontinuity, is still below the "two-dimensional critical temperature." The isotherm at 131.3°K. has a much shorter discontinuity that indicates its proximity to the critical temperature. The isotherm at 136.0° K. has no instantaneous vertical slope,[8] and is above the critical temperature. These three isotherms therefore show critical temperature phenomena in the behavior of the adsorbed film of ethane on sodium chloride.

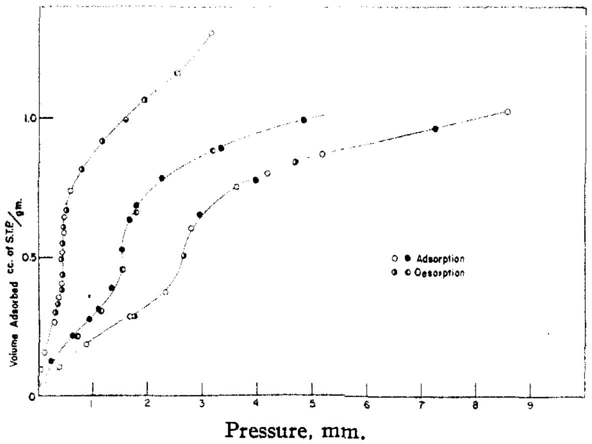

Fig. 1.—Adsorption and desorption of ethane on cube crystals of sodium chloride, at 122.9, 131.3 and 136.0°K.

The two-dimensional critical temperature of ethane on sodium chloride is less than half of the normal three-dimensional critical temperature. This type of behavior has been described by de Boer,[9] as to be expected from the introduction of an induced dipole moment on the ethane molecule from the ionic surface. To cause such a lowering of the two-dimensional critical temperature, the dipoles must be oriented parallel to each other. A diagram illustrating the arrangement of the condensed phase of ethane on a sodium chloride substrate was published by Ross[7] in 1948, and embodies an implicit prophecy of this requirement. Each molecule of ethane is depicted on the crystal lattice in an identical position with respect to the surrounding positive and negative ions. The induced dipoles would therefore necessarily be parallel to one another.

Experimental.—The sodium chloride sample was prepared by the method of Craig and McIntosh.[10] The temperature control was effected by a cryostat based on a design by J. A. Morrison.[11] The ethane was Matheson Research Grade, further purified by passing through *Ascarite* and concd. H_2SO_4 and then fractionated twice into a storage bulb.

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[7] S. Ross, THIS JOURNAL, **70**, 3830 (1948).

[8] J. R. Partington, "Advanced Treatise on Physical Chemistry," Vol. I, Longmans, Green and Co., London, 1949, p. 628.

[9] J. H. de Boer, "The Dynamical Character of Adsorption," Clarendon Press, Oxford, 1953, pp. 168–169.

[10] A. Craig and R. McIntosh, *Can. J. Chem.*, **30**, 448 (1952).

[11] J. A. Morrison, private communication.

DEPARTMENT OF CHEMISTRY HADDEN CLARK
RENSSELAER POLYTECHNIC INSTITUTE
TROY, N. Y. SIDNEY ROSS

RECEIVED OCTOBER 28, 1953

LONG RANGE MIGRATION OF CHEMICAL ACTIVITY IN THE SOLID STATE

Sir:

In a study of the chemical effects of the irradiation *in vacuo* of solid polyethylene in the heavy water pile of the Argonne National Laboratory, it has been found that the concentration of vinylidene groups, of which the total unsaturation of the unirradiated polyethylene is constituted—one vinylidene group per molecule—decreases linearly with time of irradiation while simultaneously the concentration of *trans*-vinylene groups increases. These results as estimated from infrared absorption studies are shown in Fig. 1.

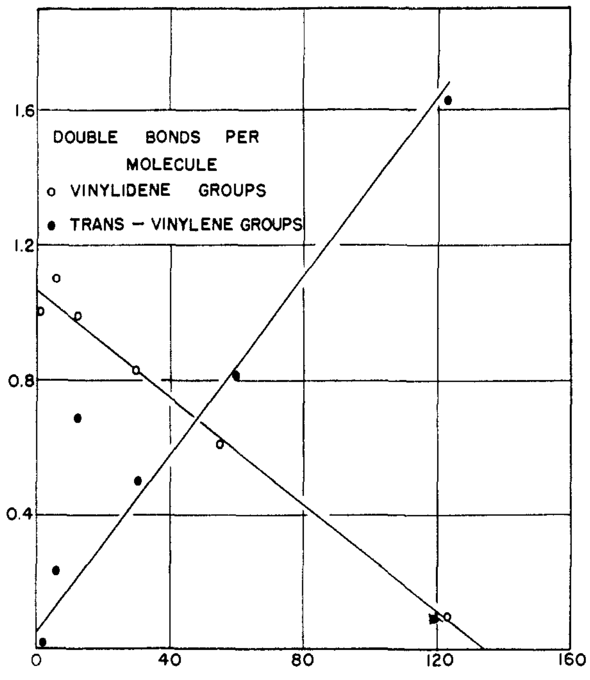

Fig. 1.

As there exists in this type of polyethylene only one vinylidene group per 2300 carbon atoms, the statistical probability of the vinylidene group being affected by the incident radiation is only two in 2300; yet the results indicate that one vinylidene group is eliminated for every 3.6 molecules of hydrogen evolved. To explain this interesting fact the hypothesis of the long range migration of chemically active centers in the polyethylene is postulated.

These chemically active centers may be either hydrogen atoms which must be produced in large numbers because of the relatively large amounts of hydrogen gas liberated, or positive or carbonium ions or free radical centers. Space does not permit a discussion as to the relative probabilities of each of these entities being the chemically active center; such discussion will be reserved for a more detailed publication. Free radicals must be produced by the abstraction by atomic hydrogen of hydrogen from the paraffinic chains of polyethylene as well as by the incident radiation or ionization produced by the irradiation; hence it is free radicals to which this discussion will be limited.

Free radicals when first formed would presumably exist for quite long periods of time as they can disappear only by reaction with other free radicals which migrate slowly through the solid polyethylene. By a "random walk" mechanism between energetically equivalent positions, the free radical centers are postulated to move along the carbon chain until localized at the vinylidene groups where an energy state estimated to be approximately 9–10 kcal./mole lower than along the hydrocarbon chain serves effectively to trap the free radical centers. These free radical centers thus activate the vinylidene groups and cause their initial rapid disappearance.

As the disappearance of the vinylidene groups follows a zero order rate law, the evidence again shows that the incident radiation is not responsible directly for this effect. The initial disappearance of the vinylidene group is also brought about by the bombardment of polyethylene with cathode rays.[1] The effect, therefore, may be a general one.

Details of this work including a description of previous work[2] on the cross-linking and unsaturation produced in polyethylene by high energy radiations, and including an application of the postulate of this note to the work of others will shortly be submitted for publication.

Grateful acknowledgment is expressed to the Visking Corporation of Chicago for financial support of this research and to the technical staff of the Argonne National Laboratory for their coöperation.

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[1] Private communication from Dr. P. H. Lindenmeyer, The Visking Corporation, Chicago.

[2] D. G. Rose, M.S. Thesis, Northwestern University, 1948; M. Dole, Report of Symposium IV, "Chemistry and Physics of Radiation Dosimetry," Army Chemical Center, Maryland, 1950, p. 120.

NORTHWESTERN UNIVERSITY MALCOLM DOLE
EVANSTON, ILLINOIS C. D. KEELING

RECEIVED NOVEMBER 2, 1953

STUDIES ON POLYPEPTIDES. V. THE SYNTHESIS OF ARGININE PEPTIDES[1]

Sir:

The amino acid L-arginine is a constituent of a number of biologically active polypeptides and methods for its incorporation into peptide structures are of considerable importance.

As far as we were able to ascertain the synthesis of low molecular weight L-arginyl peptides, *i.e.*, peptides in which the carboxyl group of L-arginine is linked to the amino group of another amino acid, has hitherto not been achieved.

We wish to present the preparation of the first three representatives of this class of compounds, namely L-arginyl-L-alanine, L-arginyl-L-phenylalanine and L-arginyl-L-tyrosine.

Carbobenzoxy-L-nitroarginine[2] served as the key intermediate in our method of synthesis. Previous attempts to convert this substance into a hydrazide or acid chloride were unsuccessful.[3] We have now observed that carbobenzoxy-L-nitroarginine forms a mixed anhydride[4,5] when it is subjected to the action of ethyl chloroformate in the presence of a tertiary amine. This mixed anhydride reacts with amines and amino acid or peptide esters to give the respective carbobenzoxy-L-nitroarginyl amides and peptide esters. In this manner carbobenzoxy-L-nitroarginine was combined with aniline to give carbobenzoxy-L-nitroarginyl anilide, m.p. 167–168°, $[\alpha]^{27}\text{D}$ −3.5° (in CH_3OH). *Anal.* Calcd. for $C_{20}H_{24}O_5N_6$: C, 56.1; H, 5.6; N, 19.6. Found: C, 56.2; H, 5.5; N, 19.7. The interaction of the mixed anhydride with the methyl esters of L-alanine, L-phenylalanine and L-tyrosine gave: (1) carbobenzoxy-L-nitroarginyl-L-alanine methyl ester, m.p. 155–157°, $[\alpha]^{25}\text{D}$ −18.8° (in CH_3OH). *Anal.* Calcd. for $C_{18}H_{26}O_7N_6$: C, 49.3; H, 6.0; N, 19.2. Found: C, 49.5; H, 5.9; N, 19.3; (2) carbobenzoxy-L-nitroarginyl-L-phenylalanine methyl ester, m.p. 131–132°, $[\alpha]^{25}\text{D}$ −8.2° (in CH_3OH). *Anal.* Calcd. for $C_{24}H_{30}O_7N_6$: C, 56.0; H, 5.9; N, 16.3. Found: C, 55.7; H, 5.7; N, 16.1; (3) carbobenzoxy-L-nitroarginyl-L-tyrosine methyl ester, m.p. 159–160°, $[\alpha]^{25}\text{D}$ −3.5° (in CH_3OH). *Anal.* Calcd. for $C_{24}H_{30}O_8N_6$: C, 54.3; H, 5.7; N, 15.8. Found: C, 54.2; H, 5.4; N, 15.9.

Saponification with aqueous sodium hydroxide converted these peptide esters into the corresponding carbobenzoxy-L-nitroarginyl peptides, *i.e.*, carbobenzoxy-L-nitroarginyl-L-alanine, m.p. 207–208°, $[\alpha]^{26}\text{D}$ −11.6° (in CH_3OH), carbobenzoxy-L-nitroarginyl-L-phenylalanine, m.p. 225–226°, $[\alpha]^{26}\text{D}$ +1.6° (in CH_3OH) and carbobenzoxy-L-nitroarginyl-L-tyrosine, m.p. 164–166°, $[\alpha]^{28}\text{D}$ +8.3° (in CH_3OH).

Hydrogenation of the carbobenzoxy-L-nitroarginyl peptides in the presence of spongy palladium in methanol containing 10% by weight of glacial acetic acid gave the crystalline diacetate salts of the respective L-arginyl peptides, namely: (1) L-arginyl-L-alanine diacetate, m.p. 173–174°, $[\alpha]^{27}\text{D}$ +12.2° (in H_2O). *Anal.* Calcd. for $C_{13}H_{27}O_7N_5$: C, 42.7; H, 7.4; N, 19.2. Found: C, 42.9; H, 7.4; N, 19.4; (2) L-arginyl-L-phenylalanine diacetate, m.p. 172–173°, $[\alpha]^{28}\text{D}$ +23.9° (in H_2O). *Anal.* Calcd. for $C_{19}H_{31}O_7N_5$: C, 51.7; H, 7.1; N, 15.9. Found: C, 52.4; H, 7.0; N, 16.1; (3) L-arginyl-L-tyrosine diacetate, m.p. 157–158°, $[\alpha]^{27}\text{D}$ +30.4° (in H_2O). *Anal.* Calcd. for $C_{19}H_{31}O_8N_5$: C, 49.9; H, 6.8; N, 15.3. Found: C, 49.6; H, 7.2; N, 15.1. The salts exhibited a positive Sakaguchi test, gave a blue color with ninhydrin, and contained no detectable quantities of ammonium acetate.

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[1] The authors wish to express their appreciation to Armour and Company and to the U.S. Public Health Service for their generous support of this investigation.

[2] M. Bergmann, L. Zervas and H. Rinke, *Z. physiol. Chem.*, **224**, 40 (1934).

[3] J. S. Fruton, "Advances in Protein Chemistry," Vol. V, Academic Press, Inc., New York, N. Y., 1949, p. 64.

[4] T. Wieland and R. Sehring, *Ann.*, **569**, 122 (1950).

[5] R. A. Boissonnas, *Helv. Chim. Acta*, **34**, 874 (1951).