control experiment seems to be needed: namely, to test the constancy of the emanating power of some other eutectic mixture, prepared in a similar manner, but consisting of salts known definitely not to form any compounds whatsoever, at any temperatures, such as the pair KCl–K_2SO_4. In experiments described by Hahn himself[1] (pp. 200–215), even pure substances, which could not be undergoing any chemical reaction, such as dried thorium oxide or iron oxide gels, show variation of the emanating power on mere standing, at various temperatures, and in various degrees of relative humidity.

Finally, Hahn and Strassmann offer the following explanation for the otherwise surprising reactivity of these dry solid salts at a temperature so far below their melting points. On the basis of the "loosening temperature" of "incipient softening," as observed by Hahn and collaborators in work with the emanation method [a phenomenon similar to the "agglomeration temperature" observed in experiments of Tammann],[5] a preliminary loosening of the crystals of a simple solid is to be expected at a temperature approximately 0.5 to 0.6 of the absolute melting point. Hahn and Strassmann then suggest that their salt mixture was evidently already in the temperature range of this preliminary loosening, inasmuch as 20° is 0.53 of the absolute melting or freezing point, 278°, of the mixture considered as a eutectic. This reasoning however involves a misconception of the meaning of Tammann's "loosening" or "agglomeration" temperature. Materials in a mixture (no matter what the proportion may be—and the proportions of a eutectic mixture are purely accidental) behave independently in respect to strictly thermodynamic properties. The temperature of the preliminary loosening of the crystal lattice is, of course, a function of the lattice itself, or of the lattice bond strengths. This property, for either of the two salts involved in a simple eutectic, remains constant and is not affected by the presence of the merely admixed crystals of the other salt. In a eutectic mixture, in short, as in any mixture of solids, we are dealing with two separate phases, each with its own thermodynamic properties, and its own crystal structure. Consequently the temperature of 20° of the experiment cannot be related to the so-called eutectic melting point but only separately, for each salt, to its own individual melting point, in the calculation of the approximate temperature at which this preliminary loosening may be expected to start; these "loosening temperatures" would then be between 37 and 98° for potassium nitrate and between 161 and 248° for barium nitrate, that is, far above room temperature.

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[5] Tammann, *Z. anorg. allgem. Chem.*, **176**, 46 (1928).

Exchange Reaction of Organic Compounds with D_2SO_4

BY RUDOLF SCHOENHEIMER, D. RITTENBERG AND A. S. KESTON

Ingold, Raisin and Wilson[1] have found that aliphatic hydrocarbons exchange hydrogen with D_2SO_4. Since this finding offered a possibility of preparing deutero compounds, we have investigated the exchange of (a) palmitic acid, (b) *dl*-alanine, (c) *d*-leucine, and (d) cholesteryl chloride dibromide. The first three compounds were dissolved in 95–99% sulfuric acid containing 25–30 atom per cent. of deuterium, and heated at 100° for twenty-four hours. The cholesterol derivative not being soluble in sulfuric acid was dissolved in carbon tetrachloride and this solution refluxed in contact with the sulfuric acid. The substances isolated contain (a) 1.78, (b) 1.30, (c) 0.86, (d) 0.03 atom per cent. of deuterium. The leucine was racemized. Neither of the amino acids on boiling with large volumes of 20% ordinary sulfuric acid in H_2O for forty-eight hours lost any of the deuterium introduced by the concentrated D_2SO_4. The fact that the deuterium content of the cholesterol derivative is so small is probably due to its insolubility in sulfuric acid.

[1] C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 1643 (1936).

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The Ratio of Substitution to Addition in the Reaction of Chlorine with Olefins in Dilute Carbon Tetrachloride Solution

BY T. D. STEWART, KENNETH DODD AND GEORGE STENMARK

Stewart and Weidenbaum[1] found 2-pentene to yield largely 1-chloro-2-pentene upon chlorination and interpreted the substitution as a reaction induced by the normal addition reac-

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[1] Stewart and Weidenbaum, THIS JOURNAL, **58**, 98 (1936).

tion. We have made some preliminary measurements of 1-pentene, 2-hexene, 1-heptene, 2-heptene and 3-heptene, with repeated measurements on a sample of the same 2-pentene used by Stewart and Weidenbaum. The identity of the substitution products has not been determined as interest lay chiefly in the magnitude of the substitution reaction as affected by the concentration of the reagents. The results are tabulated, giving the ratio of hydrogen chloride formed to the moles of chlorine reacted as the per cent. substitution.

TABLE I

PER CENT. SUBSTITUTION IN THE REACTION OF CHLORINE WITH VARIOUS OLEFINS IN CARBON TETRACHLORIDE

Initial concentrations moles/liter		
1-Pentene	Chlorine	% substitution
0.073	0.065	9.3
.010	.010	12.8
.110	.048	9.7
.055	.0260	14.1
.016	.006	17.1
.157	.038	10.6
.079	.015	16.1
.184	.019	13.1
.043	.092	6.9
1-Heptene	Chlorine	
0.251	0.266	17.2
.050	.051	13.5
.334	.178	20.3
.0667	.0342	15.0
.436	.0836	22.0
.0800	.0205	16.4
2-Heptene	Chlorine	
0.265	0.320	11.3
.249	.266	10.2
.050	.0557	7.4
.067	.0405	9.0
.416	.087	13.0
.080	.0204	11.5
.167	.348	8.0
3-Heptene	Chlorine	
0.0785	0.0545	12.0
2-Hexene		
0.0498	0.0545	11.5
.0665	.0365	12.2
2-Pentene		
0.0368	0.0492	45.2
.0526	.0238	58.7

In general the same effect of the ratio of the concentrations of the reactants as observed by Stewart and Weidenbaum is noted, *i. e.*, excess olefin increases substitution and excess chlorine decreases substitution. This is superimposed upon an effect due to actual concentration. In the case of 1-pentene more dilute systems give increased substitution, whereas with the heptenes just the opposite occurs. While the effect of changes in the ratios of the reactants and in their concentrations seems small in these cases as compared to 2-pentene, it is interesting to observe that the per cent. change in the per cent. substitution in all cases is comparable.

The actual rates of reaction are roughly in the order 2-pentene $>$ 3-heptene, 2-hexene, 2-heptene $\gg$ 1-pentene $>$ 1-heptene. The half life of the 1-heptene reaction with the reactants initially at 0.01 M is approximately one hundred minutes, while the reactions involving 2- and 3-heptene were complete within thirty seconds and the reaction of 2-pentene is too rapid to estimate. In the case of 1-pentene and chlorine each at 0.1 M, the reaction is 65% complete in two minutes and this indicates a specific reaction rate about tenfold greater than that of 1-heptene. It would appear then that large differences in reactivity do not greatly affect the ratio of addition to substitution when the reactivity is moderately large, but there remains the fact that a very high per cent. substitution is found in the case of the unusually reactive olefin, as noted by Stewart and Weidenbaum.

Experimental.—The procedure in general was that already described.[1] 1-Pentene, b. p. 29.9–30.1°, was prepared as described by Sherrill.[2] Within the two minutes allowed for this series, the reactions were 60–85% complete with respect to chlorine, and in that time loss of hydrogen chloride by addition to excess olefins was negligible. 1-Heptene, b. p. 93.0°, n^{25}D 1.3965, was prepared and purified as described by Kistiakowsky.[3] Time of reaction varied from one to fifteen minutes. Mixtures of the isomers of 2-heptene, b. p. 97.6°, n^{25}D 1.4021, and 2-hexene, b. p. 68.0–68.2°, were prepared by the β-bromo ether method.[4] The time of reaction in these cases was thirty seconds. In all cases final distillation of the olefin was from metallic sodium.

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[2] Sherrill, THIS JOURNAL, **56**, 926 (1934).

[3] Kistiakowsky, *ibid.*, **58**, 137 (1936).

[4] Schmitt and Boord, *ibid.*, **54**, 751 (1932).