The effect of inert gases on the rate of reaction also indicates that the decomposition does not follow the chain mechanism:

$$\begin{array}{rlccc} CH_3CHO & \longrightarrow CH_3 + CHO & k_1 & E_1 & (1) \\ CH_3 + CH_3CHO & \longrightarrow CH_4 + CH_3CO & k_2 & E_2 & (2) \\ CH_3.CO & \longrightarrow CH_3 + CO & k_3 & E_3 & (3) \\ 2CH_3 & \longrightarrow C_2H_6 & k_4 & E_4 & (4) \\ 2CH_3 + M & \longrightarrow C_2H_6 + M & k_5 & E_5 & (5) \end{array}$$

but rather the direct rearrangement

$$CH_3CHO \longrightarrow CH_4 + CO \quad k_6 \quad E_6 \quad (6)$$

for whereas at temperatures above 440°, the recombination of methyl radicals is mainly a homogeneous reaction which takes place partially at ternary collisions so that the rate of the chain reaction is retarded by helium,[7] the thermal decomposition of acetaldehyde itself is accelerated by nitrogen,[8] and by helium (Table I).

TABLE I

TEMPERATURE 552°

$p_{\text{Acet.}}$, mm.	p_{He}, mm.	$t^1/_3$, sec.	$t^1/_2/t^1/_3$	Increase in $1/t^1/_3$, %
93.9	429	148	1.97	11
82.0	375	160	1.95	10
96.4	...	163	1.94	..
83.0	...	175	1.93	..

The last column of Table I gives the increase in rate (as determined from values of the time taken for the pressure to increase by one-third of the initial pressure of acetaldehyde) in the presence of helium compared to the rate for the same initial pressure of pure acetaldehyde.

The results with helium were obtained with the same experimental procedure as that for which it was found that the rate of the chain decomposition in the presence of ethylene oxide was retarded by about 10% at 441° for a 2:1 helium ratio.[7] As the heterogeneous recombination of methyl radicals decreases with temperature, the acceleration given in Table I cannot be accounted for by the inert gas preventing the diffusion of radicals to the walls. Neither can it be explained on the chain mechanism by an increase in the rate of production of methyl radicals such as might occur if reaction 1 were second order; for the initial rate of the chain mechanism is

$$-(dp/dt) = p^{(n/2)+1}\, k_2 \sqrt{k_1/[k_4 + k_5\,(M)]} \quad (1)$$

where n is the order of reaction 1, so that to explain the observed order of approximately 1.5, Reaction 1 has to be first order.

As the chain mechanism competes so ineffectively with the direct rearrangement, it may be assumed that its over-all energy of activation, $E_{\text{ald.}}$, is considerably higher. If the variation with temperature of the recombination of free radicals at ternary collisions can be neglected, then, from equation 1, $E_{\text{ald.}} = E_2 + {}^1/_2(E_1 - E_4)$. Values of $(E_2 - {}^1/_2E_4)$ may be obtained from the decompositions induced by azomethane and ethylene oxide; from the results with azomethane, Allen and Sickman[3] derived the value 13,800 cal. on the assumption, which is probably justified,[9] that all the azomethane decomposes to give free radicals. With ethylene oxide the fraction of molecules which gives free radicals is approximately 14%;[7] if the temperature independent factors are the same for both types of decomposition, such a proportion would be obtained if the energies of activation differ by about 3000 cal., *i. e.*, that for the production of free radicals would be approximately 56,000 cal. Making a calculation similar to that for azomethane, $(E_2 - {}^1/_2E_4)$ is therefore 13,500 cal., in good agreement with the value from azomethane. Thus $E_{\text{ald.}} \simeq {}^1/_2E_1 + 13{,}700$ cal., so that for the chain mechanism to have a larger energy of activation than that actually observed (50,000 cal.[10] or 45,700 cal.[11]), the energy of activation (E_1) for the breaking of the C–C bond must be closer to 80,000 cal. than to the value of 70,000 cal. assumed by Rice and Herzfeld.

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[7] Fletcher and Rollefson, THIS JOURNAL, **58**, 2135 (1936).

[8] Hinshelwood and Askey, *Proc. Roy. Soc.* (London), **A128**, 91 (1930).

[9] O. K. Rice and Sickman, *J. Chem. Phys.*, **4**, 242 (1936).

[10] Fletcher and Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 41 (1933).

[11] Letort, *Compt. rend.*, **199**, 1617 (1934).

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The Standard Electrode Potential of Silver

BY J. J. LINGANE AND W. D. LARSON

The value for the standard potential of the silver electrode, Ag | Ag^+ ($a = 1$), given by Lewis and Randall[1] is −0.7995 v., whereas the value given in the "International Critical Tables"[2] is −0.7978 v. Both of these values apparently are based on the measurements of Noyes and Brann[3] on cells involving liquid junction potentials. Evaluation of the standard potential of the silver electrode from these measurements

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[1] Lewis and Randall, "Thermodynamics," McGraw Hill Book Co., Inc., New York, 1923, p. 414.

[2] "International Critical Tables," Vol. VI, p. 333.

[3] Noyes and Brann, THIS JOURNAL, **34**, 1016 (1912).

necessitates the use of the standard potential of the calomel electrode, and the difference between the two values given above apparently is due to the revision of the accepted value of the standard potential of the calomel electrode.

We wish to call attention to a simple unambiguous method by means of which the standard electrode potential of silver may be calculated from the standard potential of the silver–silver chloride electrode, Ag | AgCl(s), Cl^- ($a = 1$), and the activity product of silver chloride. The relation between the standard potential of the silver–silver chloride electrode, E^0_{AgCl}, the activity product of silver chloride, K, and the standard potential of the silver electrode $E^0_{Ag,\,Ag^+}$, is given by the thermodynamic equation

$$E^0_{AgCl} = E^0_{Ag,\,Ag^+} - (RT/F)\ln K \qquad (1)$$

The value of E^0_{AgCl} has been determined by several investigators[4] from measurements of the cell H_2 | HCl, AgCl(s) | Ag. A critical examination of the data of these authors has led us to believe that the measurements of Carmody, who used quartz cells and was the only one of these investigators who was able to obtain very concordant results in extremely dilute solutions, are the most reliable. By graphical extrapolation Carmody obtained the value −0.2223 v. for E^0_{AgCl}. We have recalculated the value of E^0_{AgCl} from Carmody's data for the three most dilute solutions (0.0007280, 0.0005518 and 0.0003288 m) by application of the limiting law of Debye and Hückel. This leads to the equation

$$E^0_{AgCl} = -E_{cell} - \frac{RT}{F}\ln m^2 + 2 \times 0.5045\frac{RT}{F}S^{1/2} \qquad (2)$$

in which S is the total ionic strength of the solution corrected for the solubility of silver chloride. This equation leads to the same value of E^0_{AgCl} for each of the three most dilute solutions, namely, −0.2222 v. at 25°. We consider this to be the most reliable value of E^0_{AgCl}, and it is in excellent agreement with the value −0.2221 v. estimated by Randall and Young.[5]

The activity product of silver chloride has been determined recently by Brown and MacInnes[6] by a highly precise electrometric titration method. They found a value of K equal to 1.721×10^{-10} at 25°, and this result is apparently reliable to a few tenths of one per cent.

By substituting these values into equation (1) we obtain for the standard electrode potential of silver at 25°

$$E^0_{Ag,\,Ag^+} = -0.2222 + 0.05913 \log (1.721 \times 10^{-10}) = -0.7996 \text{ v.}$$

The close agreement between this result and the value given by Lewis and Randall is remarkable in view of the fact that the value calculated above is based on entirely independent measurements by different investigators. This result therefore constitutes strong evidence in favor of accepting the value −0.7996 v. as the standard potential of the silver electrode, rather than the value −0.7978 v. given in the "International Critical Tables."

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[4] (a) Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917); (b) Linhart, *ibid.*, **41**, 1175 (1919); (c) Scatchard, *ibid.*, **47**, 708 (1925); (d) Nonhebel, *Phil. Mag.*, [7] **2**, 1085 (1926); (e) Carmody, THIS JOURNAL, **54**, 188 (1932).

[5] Randall and Young, *ibid.*, **50**, 989 (1928).

[6] Brown and MacInnes, *ibid.*, **57**, 459 (1935).

Beta-Octyl Thiocyanate

BY W. GORDON ROSE AND H. L. HALLER

In the course of studies on the relative toxicity to insects of optical isomers of secondary alkyl thiocyanates, the results of which will be reported elsewhere, occasion has been had to prepare the dextro and levo forms of beta-octyl thiocyanate (alpha-methylheptyl thiocyanate). By the action of phosphorus tribromide (138.0 g.) on dextro-beta-octanol (66.0 g.), $[\alpha]^{20}\text{D}$ +9.70° homogeneous, $[\alpha]^{20}\text{D}$ +11.88° in ethanol ($c = 5.67$), there was obtained 81.3 g. of beta-octyl bromide, $[\alpha]^{20}\text{D}$ −32.15° homogeneous, $[\alpha]^{20}\text{D}$ −45.30° in ethanol ($c = 5.99$). The latter (81.0 g.), on being refluxed in 100 cc. of methanol with 45.0 g. of potassium thiocyanate, yielded 51.7 g. of beta-octyl thiocyanate, b. p. 98.5–99.0° at 4 mm., d^{20} 0.919, $n^{20}\text{D}$ 1.4635, $MR\text{D}$(obsd.) = 51.30, $MR\text{D}$(calcd.) = 51.09, $[\alpha]^{20}\text{D}$ +51.7° homogeneous, $[\alpha]^{20}\text{D}$ +59.1° in ethanol ($c = 5.06$). *Anal.* Calcd. for $C_9H_{17}NS$: C, 63.08; H, 10.01; N, 8.18. Found: C, 63.14, 63.17; H, 10.02, 10.08; N, 8.44, 8.32.

Beta-octyl thiocyanate has been obtained previously by the interaction of beta-octyl-*p*-toluenesulfonate and potassium thiocyanate.[1] The beta-octyl sulfonate was obtained on oxidation of the corresponding sulfinate, which in turn

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[1] Kenyon, Phillips and Pittman, *J. Chem. Soc.*, 1081 (1935).