Å, $b = 12.88$ Å, $c = 14.34$ Å, $\beta = 101.5°$. There are four formula units per unit cell; density, calc. 2.23, found 2.23 g/cm³. The space group, from systematic absences, is $P2_1/c$ (No. 14). The crystals are isomorphous with those of the corresponding ethylenethiourea compound.[2]

Bromo(phenyl)trimethyleneselenoureatellurium(II), $C_6H_5Te(trsu)Br$, was prepared using 1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.41 g) of trimethyleneselenourea dissolved in 10 ml of warm methanol. 1.25 mmol of bromine dissolved in 2.58 ml of methanol was added. The resulting clear orange red solution was placed at room temperature for 2 h. Yield, 0.83 g (74 %). M.p. 152–153 °C. (Found: C 26.86; H 2.84; N 6.19; Br 17.91. Calc. for $C_{10}H_{13}N_2SeTeBr$: C 26.80; H 2.90; N 6.25; Br 17.85).

The compound forms yellow monoclinic prisms and plates, the prisms are extended along the *a* axis. The unit cell dimensions are $a = 9.04$ Å, $b = 15.99$ Å, $c = 10.53$ Å, $\beta = 120.8°$, and there are four formula units per unit cell; density, calc. 2.27, found 2.25 g/cm³. The space group, from systematic absences, is $P2_1/c$ (No. 14).

Chlorobis(ethyleneselenourea)phenyltellurium(II), $C_6H_5Te(esu)_2Cl$, was prepared from 1.25 mmol (0.5 g) of diphenylditelluride and 5.4 mmol (0.8 g) of ethyleneselenourea dissolved in 15 ml warm methanol, adding 1.25 mmol of chlorine dissolved in 2.25 ml of tetrachloromethane. The resulting clear orange-red solution was placed at room temperature for 4 h. Yield, 0.93 g (68 %). M.p. 190–191 °C (dec.). (Found: C 26.71; N 10.32; Cl 6.67. Calc. for $C_{12}H_{17}N_4Se_2TeCl$: C 26.75; H 3.16; N 10.40; Cl 6.59).

The crystals are orange-red orthorhombic prisms extended along the *c* axis, with $a = 13.56$ Å, $b = 15.43$ Å, $c = 8.52$ Å. There are four formula units per unit cell; density, calc. 2.01, found 2.02 g/cm³. The space group, from systematic absences, is $P2_12_12_1$ (No. 19).

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Received December 6, 1974.

Distribution of Tritium Labeling between Alternative Sites in Carbon Compounds

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The tritium labeling of carbon compounds leads usually to more than one product. Specific labeling is possible only if the replaceable protons differ greatly by their acidities. In other cases, however, an analysis of the products would be highly desirable but suitable methods for this kind of analysis have not been available. This paper reports a method which is based on the formal kinetics of the detritiation reactions. Labeled phenyl-2-propanone (I) was

$$\overset{a}{C_6H_5}-\overset{}{CH_2}-\overset{O}{\overset{\|}{C}}-\overset{b}{CH_3} \quad (I)$$

chosen as an example. Preliminary experiments indicated that the nonaromatic hydrogens of this compound were acidic enough to display isotope exchange reactions even in slightly alkaline solutions. In addition, the difference between the rates of the exchange reactions occurring at the two nonequivalent reaction sites was sufficient to make the kinetic analysis possible.

Tritiation of phenyl-2-propanone (Fluka) took place as follows. A mixture of 10^{-5} m³ of the ketone, 3×10^{-5} m³ of 100 mol m^{-3} sodium hydroxide, and 10^{-9} m³ of tritiated water (this amount of water had an activity of about 10^7 s^{-1}) were vigorously agitated at room temperature for 20 h, and the ketone was then extracted into diethyl ether. The ether was subsequently distilled off, and the remaining ketone was distilled under reduced pressure, b.p. 344 K at 0.40 kPa. The purity of the product (denoted by A) was ascertained by NMR spectroscopy. Its activity was 7.5×10^{11} s^{-1} m^{-3}. As will be shown later, about 57 % of the labeling was at the methylene group. The higher labeling of the methylene hydrogens must be the result of kinetic control, these hydrogens being obviously more acidic than those of the methyl group. In the case of thermodynamic control, at the final equilibrium, only 40 % of the labeling would be at the methylene hydrogens. This suggested that even higher labeling at the methylene group might be achieved by shortening the reaction time. Accordingly, the product (denoted by B) obtained after only 2 h reaction time gave an activity of 5×10^{11} s^{-1} m^{-3} with about 90 % of the label at the methylene group. When 3×10^{-6} m³ of product A was stirred at room

Table 1. Detriatiation of phenyl-2-propanon at 298.15 K in aqueous sodium hydroxide. k_a and k_b are the rate coefficients for detritiation from the methylene and methyl groups, respectively, and x is the fraction of tritium labeling initially present at the methylene group. The errors given are standard errors.

Sample	$k_a/10^{-5}$ mol^{-1} m^3 s^{-1}	$k_b/10^{-6}$ mol^{-1} m^3 s^{-1}	x
A	8.16	3.85	0.570±0.003
	8.51	3.90	0.574±0.002
B	8.27	3.84	0.909±0.002
	8.87	4.39	0.899±0.003
C	8.41	3.78	0.441±0.002
	9.52	3.83	0.438±0.002
D = 2B + 1C	7.88	3.65	0.759±0.002
	7.62	3.67	0.759±0.002
E = 1B + 2C	8.28	3.84	0.610±0.002
	8.14	3.84	0.608±0.002
	av. 8.37±0.17	3.86±0.06	

temperature with 10^{-5} m^3 of 100 mol m^{-3} sodium hydroxide for 2 h the product (denoted by C) thus obtained gave a total activity of 5×10^{11} s^{-1}m^{-3} with only 44 % methylene labeling. Higher activity at the less acidic site at the expense of the labeling at the more acidic site could thus be effected by partial detritiation of the labeled product.

The kinetic measurements were made at 298.15±0.05 K in 100 mol m^{-3} aqueous sodium hydroxide. The aliquots, 5×10^{-6} m^3, withdrawn from the reaction mixture were run into 2×10^{-6} m^3 of 300 mol m^{-3} sulfuric acid. The sample solution were saturated with sodium phosphate and the ketone was extracted into 10^{-5} m^3 of anisole. The samples, 5×10^{-6} m^3, were then pipetted from the organic layer and transferred to vials containing 10^{-5} m^3 of the scintillation liquid (0.25 g of *p*-bis(*o*-methylstyryl)benzene and 10 g of diphenyloxazole in 2.5×10^{-3} m^3 of toluene). The analysis was performed on a Wallac 81000 scintillation counter. In these runs the first 4 – 5 samples were taken as fast as possible in order to extrapolate the count rates to the zero time. Thereafter, about thirty samples were taken during the progress of the reaction. The final samples were taken after the slower detritiation reaction had continued for about ten half lives.

Since two parallel reactions are involved, the apparent first-order rate coefficients decrease with time. In order to calculate the true rate coefficients of the individual reactions and the radiochemical composition of the substrate, the experimental data were fitted to eqn. (1), where N_0 is the activity at the beginning

$$(N_0 - N_t)/(N_0 - N_\infty) = x[1 - \exp(-k_a't)] + (1-x)[1 - \exp(-k_b't)] \quad (1)$$

of the reaction, N_t is the activity at time t, and N_∞ is the final activity. A similar equation has previously been used for the determination of the isomeric composition of certain cyclic compounds.[1] In eqn. (1) k_a' is the first-order rate coefficient for the detritiation from carbon *a* (see I) and k_b' the corresponding rate coefficient for the detritiation from carbon *b*. The fraction of the labeling at carbon atom *a* at the beginning of the reaction is denoted by x. The parameters x, k_a', and k_b' with standard errors were calculated from the experimental data on a Univac 1108 computer using the method of least squares.[2] Kinetic data for phenyl-2-propanone are collected in Table 1. In addition to the labeled samples A, B, and C (see above), two mixtures of B and C were also studied.

The results from the kinetic study can be summarized as follows: The measured rate coefficients k_a and k_b (coefficients k_a' and k_b' divided by the hydroxide ion concentration) are independent of the tritium distribution in the sample analyzed. The standard errors of the mean values of k_a and k_b are less than 2 %, and thus their effect on the x-values cannot be significant. Accordingly, parallel experiments are seen to give almost equal x-values. Finally, the x-values measured for mixtures D and E, which were mixed up of products B and C, are in good agreement with the known compositions of the mixtures. The calculated x-value for the mixture D is 0.749, which is only 1.3 % lower than the directly measured value shown in Table 1, and that for mixture E is 0.594, which is 2.5 % lower than the measured value.

The present data clearly indicate that the kinetic method described can be applied for the determination of the relative tritium activities at separate sites in certain carbon compounds. However, it is obviously not applicable in cases in which the labeling is at more than two sites, as the increased number of parameters

makes their experimental evaluation impossible. On the other hand, the acid strengths of the hydrogens in question cannot be a limiting factor; for less acidic compounds more basic media can be used in the kinetic measurements involved.

Acknowledgement. Financial aid from the Finnish Academy, Division of Sciences, is gratefully acknowledged.

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Received November 5, 1974.

Electrolytic Nitrogen Fixation in a Molten Salt

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Electrolytic reduction of nitrogen in the presence of transition metal complexes has recently been reported.[1,2] In the most successful version, a solution of titanium tetraisopropoxide, aluminium isopropoxide, naphthalene and tetrabutylammoniumchloride in 1,2-dimethoxyethane was electrolysed under an atmosphere of nitrogen. Up to 6.1 mol NH_3 was produced per mol titanium.[1b]

In the early electrolytic experiments it was evident that the solvent (tetrahydrofuran, THF) was partially decomposed, giving tarry deposits on the electrodes. In addition to being ideal solvents for electrolytic reactions, molten salts should generally be more stable than most organic solvents. We have therefore investigated the electrolytic reduction of molecular nitrogen in a molten mixture of aluminium chloride, potassium chloride, and sodium chloride containing titanium chloride. Quantitative data from two representative experiments are given in Table 1.

The electrolysis cell was equipped with a platinum cathode and an aluminium anode. In order to avoid chemical reduction by aluminium metal (*cf.* Ref. 3) the electrode compartments were separated by two consecutive glass filters. During electrolysis, approximately the required amount of aluminium was dissolved at the anode (Table 1). No chlorine was evolved. When molecular nitrogen was bubbled through the cell during the electrolysis, reduction occurred as evidenced by the formation of ammonia on hydrolysis of the electrolyte. No ammonia was detected if the electrolysis was performed under helium or if titanium tetrachloride was omitted. Hydrazine could not be detected by qualitative tests. Reduction of molecular nitrogen to the ammonia stage started when approximately 2 F per mol of titanium had been passed through the cell. This is in accordance with van Tamelen's suggestion that titanium(II) is the active catalytic species.[4] A maximum yield of ammonia (0.25 mol/mol Ti) was obtained at 4–6 F per mol titainum, then the yield decreased slowly. Electrolytic deposition of titanium on the cathode is insufficient to explain the relatively low maximum yield. A possible explanation for the observed maximum yield of ammonia is that titanium metal separates from the molten phase due to the equilibrium (I) which is strongly displaced towards Ti(0).[5]

$$3\ \mathrm{Ti(II)} \rightleftharpoons 2\ \mathrm{Ti(III)} + \mathrm{Ti(0)} \qquad (1)$$

Another possible but hypothetical explanation is that the reduced titanium-nitrogen species is in equilibrium with molecular nitrogen according to eqn. (2). The existence

$$2\ \text{"TiN"} \overset{\mathrm{Al(III)}}{\rightleftharpoons} 2\ \text{"Ti"} + 2\ \mathrm{AlN} \rightleftharpoons N_2 + 2\mathrm{Al(0)} \qquad (2)$$

of such an equilibrium is indicated by a rough calculation using Volpin's data on the titanium catalysed reduction of molecular nitrogen by aluminium metal in molten aluminium bromide[3] (see Table 2). Reduction of nitrogen to ammonia and of titanium(IV) to titanium(0) does not account for all the current consumed. A reasonable explanation would be cathodic reduction of aluminium(III). However, no aluminium was deposited on the cathode during the electrolysis.

Table 1. Experimental data.

Exp. No.	$TiCl_4$ mmol	Current mF	NH_3 found after hydrolysis, mmol	Current yield for the oxidation of Al at the anode %
1	19	131	4.6	82
2	21	274	4.1	75