under consideration. $f^{\pm}_{trans}$, $f^{\pm}_{rot}$, $f^{\pm}_{vib}$ are the corresponding partition functions of the activated state of the ion or molecule, with the understanding that the translational degree of freedom of the activated state in the direction of diffusion has been removed. It is generally assumed that $(f^{\pm}_{vib}/f_{vib}) = 1$ for transport processes. If we consider the intermolecular translational motion as free translation in a "cage," $(f^{\pm}_{trans}/f_{trans})$ should be approximately equal to $h/[(2\pi mkT)^{1/2}V_f^{1/3}]$, where V_f is equal to the "free-volume" of each "cage." This consideration would suggest to us the definition of activation energy as $-R\mathrm{d}[\ln(D/T^{1/2})]/\mathrm{d}(1/T)$ according to equation (7). On the other hand if the intermolecular translational motion can be considered as harmonic oscillation with frequency ν such that $h\nu \ll kT$, then $(f^{\pm}_{trans}/f_{trans})$ becomes $(1 - e^{-h\nu/kT}) \cong h\nu/kT$ which suggests defining the activation energy as $-R\mathrm{d}(\ln D)/\mathrm{d}(1/T)$ according to equation (7). Since the actual intermolecular translational motion in liquid water is neither free translation nor a harmonic oscillation of frequency ν such that $h\nu \ll kT$, it appears that a correct definition of activation energy should be $-R\mathrm{d}[\ln(DT^{\gamma})]/\mathrm{d}(1/T)$ with $-1/2 < \gamma < 0$. Actually the value of $h\nu/kT$ for liquid water at 25° is about 0.97. Thus if we consider the intermolecular translational motion as harmonic oscillation we would get a value of γ that is very close to $-1/2$. However, because of the semi-crystalline structure of liquid water the potential barrier hindering the rotation of a water molecule in its normal state must be higher than that for the activated state. This would mean that the exponential index of T in f_{rot} may be higher than that in $f^{\pm}_{rot}$ which suggests that the unknown index γ in the above discussion may be higher than the value estimated above. Thus it is clear from these considerations that an exact determination of the activation energy for tracer-diffusion is still beyond our reach, but the definition $E = -R\mathrm{d}(\ln D)/\mathrm{d}(1/T)$ appears to be more plausible than the definition $E = -R\mathrm{d}[\ln(D/T)]/\mathrm{d}(1/T)$.

DEPARTMENT OF CHEMISTRY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT RECEIVED NOVEMBER 19, 1951

The Use of Chlorine Trifluoride as a Fluorinating Agent

BY EUGENE G. ROCHOW AND IRA KUKIN

The commercial availability of chlorine trifluoride[1] made it desirable to investigate the possibility of using this compound instead of elementary fluorine in a number of reactions in which that element customarily is used. In the only published work concerning the use of chlorine trifluoride as a fluorinating agent[2] HgF_2, AgF_2, CuF_2, TiF_3, PtF_4 and PbF_3 (not PbF_4) were prepared by heating the free metal with chlorine trifluoride for three hours at 120°; CoF_3 is reported from Co_3O_4 and from $CoCl_2$ without details.[3]

(1) Harshaw Chemical Company, Cleveland, Ohio.

(2) W. Huckel, *Nachr. Akad. Wiss. Gottingen Math. physik-Klasse*, 36 (1946).

(3) J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950.

Experimental

Preparation of Metal Fluorides.—Cobalt(III) fluoride, nickel(II) fluoride and silver(II) fluoride were prepared from cobalt(II) chloride, nickel(II) chloride and silver chloride, respectively. Fifty grams of the chloride first was heated in a porcelain dish for several hours at 250° to dry it, and then the anhydrous chloride was ground to pass a 30 mesh screen, and the powder was spread on a monel tray shaped to fit within a monel tube. The monel reaction tube (see Fig. 1) was similar in design to that used by Priest,[4] who designed it for the preparation of anhydrous metal fluorides by the action of free fluorine on metal chlorides.

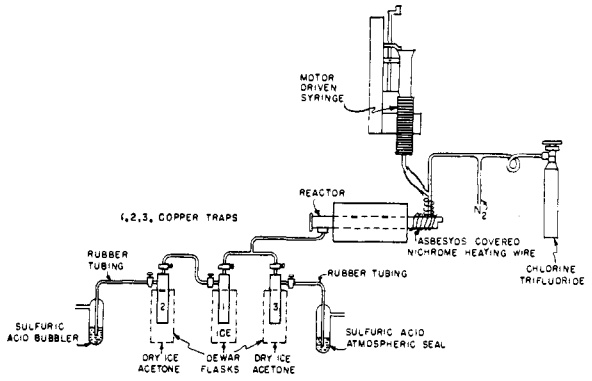

Fig. 1.—Complete apparatus assembly for preparation of fluorocarbons.

Nitrogen was passed through the reactor assembly of Fig. 1 and the furnace was heated to 250°. The flow of nitrogen was discontinued, the safety seal[4] was put in place, and the flow of chlorine trifluoride begun. During the fluorination, chlorine passed through the cold copper trap 3, and then bubbled out through the sulfuric acid outlet. The valve leading to copper trap 1 was kept closed during this fluorination cycle. The completion of the reaction was observed by the discontinuation of bubbles in the sulfuric acid outlet, since the trap was maintained at a temperature sufficiently low to condense the chlorine trifluoride (b.p. +11.3°) but not the chlorine (b.p. −33.7°).

The chlorine trifluoride then was purged from the system with dry nitrogen, and the reactor assembly was cooled. In the case of the cobalt(III) fluoride, the product was used directly for the fluorination of hydrocarbons. Its oxidizing value was determined by the oxidation of potassium iodide in caprylene[5] and was found to correspond to 90% CoF_3; the impurity was shown to be cobalt difluoride by a negative chloride test on the product. Prolonged fluorination with the chlorine trifluoride beyond the point of disappearance of chlorine at the outlet resulted in a product having an oxidizing value equal to that calculated for CoF_3.

It was found that the same reactor assembly could be used for fluorinating hydrocarbons. To do this, the valve leading to trap 3 was closed and the valves to traps 1 and 2 were opened; the hydrocarbons could then be introduced through a separate opening on the inlet tube of the reactor, by way of a metal valve. Several methods[6] for the introduction of the hydrocarbons were tried, but the use of a motor-driven syringe[7] proved most expedient. Alternation of the hydrocarbon feed and the chlorine trifluoride then allowed the same sample of cobalt fluoride to be used repeatedly without removing it.

The copper tubing and that portion of the reactor which extended in front of the electric furnace were wound with nichrome resistance wire to ensure volatilization of the hy-

(4) "Inorganic Syntheses," Vol. III, p. 171–183. See also Vol. VII-1 of the National Nuclear Energy Series, "Fluorine Technology," edited by Slesser and Schram (McGraw-Hill Book Co., Inc., New York, N. Y., 1951).

(5) Private communication from the Harshaw Chemical Company.

(6) R. D. Fowler and W. B. Burford: "Fluorocarbons," O.T.S. Report, Department of Commerce, Washington, D. C., 1947; *Ind. Eng. Chem.*, **39**, 292, 319, 329, 338, 350 (1947).

(7) This device is based in part on the automatic titrator designed by J. J. Lingane, *Anal. Chem.*, **20**, 285 (1948).

drocarbons before reaching the layer of cobalt trifluoride. The amount of hydrocarbon introduced during each cycle necessarily was somewhat less than the theoretical amount which could be fluorinated completely, based on the amount of cobalt trifluoride present, its oxidizing value, and the particular hydrocarbon used. The spent cobalt difluoride then was reoxidized with chlorine trifluoride, after the system had been flushed thoroughly with nitrogen. In this cycle the valve leading to trap 1 was kept closed while the valve to trap 3 was opened. Passing the chlorine trifluoride over the cobalt difluoride for only five minutes resulted in a conversion to the cobalt III fluoride, with an oxidizing value greater than 90% of theoretical.

It might be thought possible to mix the vapors of chlorine trifluoride and hydrocarbon and to pass the mixture over cobalt trifluoride to effect fluorination. However, it was found that if the chlorine trifluoride were mixed directly with the hydrocarbon, either as vapor in the reactor tube or as liquid in the copper traps at Dry Ice temperature, only tarry and carbonaceous material resulted. The repetitive batch process of fluorination with CoF_3 must therefore be used.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MASS. RECEIVED SEPTEMBER 12, 1951

COMMUNICATIONS TO THE EDITOR

THE ORIGINS OF GLUCURONIC ACID

Sir:

The observations that three-carbon compounds, such as lactate and pyruvate, stimulate glucuronic acid synthesis *in vitro* to a greater extent than six-carbon compounds, such as glucose, suggests that the former are either precursors of glucuronic acid or that their oxidation supplies energy for the reactions by which conjugated glucuronides are synthesized from other sources.[1]

In an attempt to clarify this problem, the synthesis of menthol glucuronic acid by liver slices of fasted guinea pigs was studied using, as substrates, glucose, and lactate, in each of which a single carbon was labeled with C^{14} as indicated in the table below. In each experiment the slices were incubated in the same modified Ringer's solution containing glucose, lactate, menthol and a sodium bicarbonate:carbon dioxide buffer system. Only one substrate was labeled in each experiment. The menthol glucuronic acid synthesized by such a system was isolated, purified to constant radioactivity and oxidized, either with periodate (which gave carbon 1, carbons 2-3-4, and carbons 5-6 as three separate fractions), or with 12% hydrochloric acid (which gave carbon 6 as a separate fraction).[2] Each fraction was isolated, specifically converted to carbon dioxide, and plated and counted as barium carbonate. The results are summarized as

Substrate	Labeled position of substrate	C-1	C-2,3,4	C-5,6
	Counts per minute per mM. carbon			
Glucose-1-C^{14}	53.8×10^5	56,500	3,200	1,320
Lactate-3-C^{14}	11.7×10^5	4,150	2,060	6,540
	8.8×10^5	830	470	1,270

It is apparent from the data with glucose-1-C^{14} that this compound enters the glucuronic acid molecule with no major redistribution of C^{14} from the 1-position of the glucose molecule. This might be interpreted as evidence for the direct conversion of glucose to glucuronic acid. However, if glucose were the sole source of glucuronic acid, it would be expected, in accordance with current concepts of glycogenesis, that symmetrical labeling of the glucuronic acid would occur when lactate-3-C^{14} was the labeled substrate. Contrary to this expectation, the average specific activity of carbons 5 and 6 of the glucuronic acid is higher than that of carbon 1, indicating that this substrate is converted to the distal portion (carbons 4, 5, 6) of the glucuronic acid molecule to a greater extent than to the proximal portion. Decarboxylation of the menthol glucuronic acid obtained with lactate-3-C^{14}, resulting in the isolation of carbon 6 as a discrete fraction, shows that practically all the radioactivity in the C-5,6 fraction resides in C-6, the specific activity of the latter being approximately 2.5 times than of C-1. It would appear from these results that the entire glucose molecule is not the sole source of the glucuronic acid. Since lactate is rapidly metabolized by pathways other than anabolic reactions, it is to be expected that considerable dilution and redistribution of the radioactivity of the original substrate will occur and will be apparent in the labeling of the menthol glucuronic acid even though lactate were a precursor.

These data, therefore, do not exclude the possibility that, in the biosynthesis of conjugated glucuronic acid, a triose, produced from lactate, condenses with another triose formed from glucose and that, in this manner, carbons 1, 2 and 3 of the glucuronic acid originate predominantly from carbons 1, 2 and 3 of glucose while carbons 4, 5 and 6 originate from a three-carbon compound. Further work, designed to test these possibilities, is in progress.

This work was done while the author was a Postdoctoral Fellow of the National Institutes of Health, U.S.P.H.S., and, subsequently, with the aid of a grant from the Nutrition Foundation, Inc. The continued guidance and assistance of Dr. Ernest Bueding and the interest of Drs. Warwick Sakami

(1) W. L. Lipschitz and E. Bueding, *J. Biol. Chem.*, **129**, 333 (1939).
(2) C. F. Huebner, R. Lohmar, R. J. Dimler, S. Moore and K. P. Link, *ibid.*, **159**, 503 (1945).