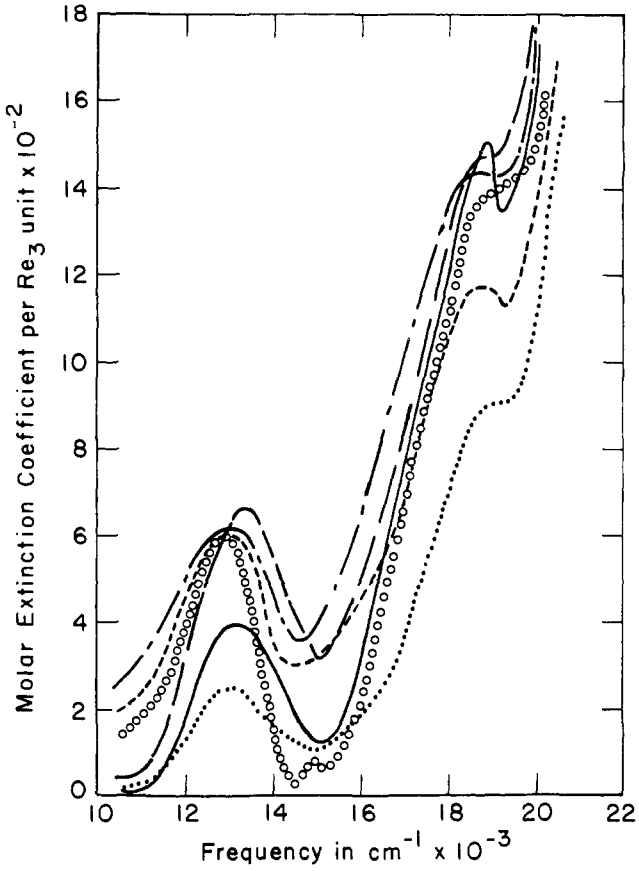

Fig. 1.—Visible spectra of rhenium(III) bromide and some derivatives. $(ReBr_3)_n$ in 48% aq. HBr (———); $(ReBr_3)_n$ in acetone (— —); $(C_5H_6N)_2Re_4Br_{15}$ in acetone (○○○○○); $(C_9H_8N)_2Re_3Br_{11}$ in aq. HBr (— · —); $[ReBr_3(C_2H_5)_2C_6H_5P]_3$ in $CHCl_3$ (·····); $[ReBr_3(C_6H_5)_3As]_3$ in acetone (. . . . .).

ion, by a single crystal X-ray study,[7] and in $Re_3Br_9[(C_2H_5)_2C_6H_5P]_3$, because the latter compound is isomorphous with $Re_3Cl_9[(C_2H_5)_2C_6H_5P]_3$, the structure of which has been determined.[3] The compounds $[ReBr_3(C_6H_5)_3As]_n$ and $(C_9H_8N)_2Re_3Br_{11}$, which have now been prepared from rhenium(III) bromide as well as solutions of rhenium(III) bromide in aqueous HBr and acetone, have visible spectra which are all very similar to one another and to the spectra of $(C_5H_6N)_2Re_4Br_{15}$ and $Re_3Br_9[(C_2H_5)_2C_6H_5P]_3$. These are shown in Fig. 1.

Not only are all of the spectra shown in Fig. 1 similar to one another, but they are quite similar to the characteristic spectrum of compounds containing the Re_3Cl_9 group.[1,3] The main difference is that in the bromo compounds strong ultraviolet absorption, presumably of Br→Re charge-transfer type, sets in at lower frequencies, and this tends to obscure the absorption band around 19,000 $cm.^{-1}$. However, the characteristic pattern of absorption is clearly the same in both the Re_3Cl_9 compounds and the rhenium(III) bromide derivatives, and is presumably characteristic of the Re_3 cluster itself.

The appearance of this characteristic spectrum in the HBr and acetone solutions of rhenium(III) bromide suggests that it consists of Re_3Br_9 units, though these may not be connected in the same way as in the chloride since the two compounds are not isomorphous.[8] A complete structure determination[9] of rhenium(III) bromide should soon provide a conclusive answer on this point.

The compound $Re_3Br_9[(C_6H_5)_3P]_3$ has also been prepared, but since no satisfactory solvent has been found, its spectrum in solution has not been recorded. However, it is isomorphous with the corresponding chloro compound whose trinuclear structure has been substantiated by spectral studies,[1] and, in addition, these $(C_6H_5)_3P$ compounds are isomorphous with $Re_3Br_9[(C_6H_5)_3As]_3$.

Finally, it may be noted that the compound $(C_9H_8N)_2Re_3Br_{11}$ is to be compared with $CsRe_3Br_{10}$, recently reported.[9] The greater size of the quinolinium ion is perhaps responsible for stabilizing $[Re_3Br_{11}]^{-2}$. A complete report on these and other compounds as well as analogs in the rhenium(III) chloride system is in preparation.[10]

(7) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, in press. The compound consists of equal numbers of Re_3Br_9 groups and $ReBr_6^{2-}$ groups. The Re_3Br_9 group has essentially the same structure as the Re_3Cl_9 groups occuring in other compounds. Its virtual symmetry is D_{3h}; the Re–Re bonds are 2.46 ± 0.01 Å. long.

(8) F. A. Cotton and S. J. Lippard, unpublished work, still in progress.

(9) J. E. Fergusson and B. H. Robinson, *Proc. Chem. Soc.*, 189 (1964).

(10) This work is being supported by the U. S. Atomic Energy Commission.

(11) N.S.F. Predoctoral Fellow 1962–1965; Woodrow Wilson Fellow (Honorary), 1962–1963.

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Appearance Potentials of the Lower Chloroalkanes

Sir:

In the mass spectrum of chloroalkanes of four or more carbon atoms, the abundance of the parent ion is almost invariably less than 1% relative to the most abundant peak.[1] It is not surprising, therefore, that electron impact estimates of the appearance potentials (A.P.) for the process

$$RCl + e \rightarrow RCl^+ + 2e \qquad (1)$$

are still unknown for the chlorobutanes.[2] Such measurements are reported here even for *t*-butyl chloride, whose parent peak has a relative abundance of 0.01%. We also record an unexpected disagreement between some of our values of A.P. and those obtained by photoionization techniques.

Our A.P. were obtained on an A.E.I. Model MS 9 mass spectrometer. The chlorides were admitted to the electron source through an unheated inlet line. Acetylene and iodomethane with A.P. of 11.41 and 9.55 e.v. were primary standards of the voltage scale[2] although other secondary standards were used as checks.[3] Conventional semilogarithmic plots of ion current against ionization voltage[4] of chloroalkane and the standard substance were compared. The peak height was usually set at 100% at 50 v., although normalizations at 14–20 v. were occasionally advantageous. In the case of *t*-butyl chloride, the ionization efficiency curves showed substantial tailing and it was necessary to compare these directly with those of the standards. Similar measurements could not be made

(1) F. W. McLafferty, *Anal. Chem.*, **34**, 2 (1962).

(2) R. W. Kiser, "Tables of Ionization Potentials," TID-6142 Report, Kansas State University, 1960, 1962.

(3) M. Baldwin, A. Maccoll, and S. L. Miller in "Advances in Mass Spectrometry," Vol. II, to be published by Pergamon Press, London, on the proceedings of a conference held in Paris, Sept., 1964.

(4) F. P. Lossing, K. U. Ingold, and I. H. Henderson, *J. Chem. Phys.*, **22**, 1489 (1954).

on neopentyl chloride as the abundance of the parent peak was found to be $\leq 10^{-4}\%$ relative to the base peak given by the *t*-butyl ion.

The A.P. of the lower chloroalkanes are given in Table I. Evidently they depend primarily on carbon

TABLE I

APPEARANCE POTENTIALS OF THE CHLOROALKANES, RCl

R	A.P.(RCl^+), e.v. E.I.[a]	A.P.(RCl^+), e.v. P.I.[b]	A.P.(CH_3CCl) − A.P.(RCl)	ΔH_f, kcal. mole^{-1} RCl[c]	ΔH_f, kcal. mole^{-1} RCl^+
CH_3	11.44 ± 0.02[d]	11.28	0	−21	243
C_2H_5	11.10 ± 0.06[e]	10.97	0.34	−26	230
n-C_3H_7	10.78 ± 0.04[f]	10.82	0.66	−32	217
i-C_3H_7	10.77 ± 0.03	10.78	0.67	−35	214
n-C_4H_9	10.50 ± 0.07	10.67	0.95	−37	205
i-C_4H_9	10.48 ± 0.1	10.66	0.94	−38	204
sec-C_4H_9	10.52 ± 0.1	10.65	0.91	−40	203
t-C_4H_9	10.3 ± 0.1	10.61	1.14	−43	195

[a] Electron impact, this work. [b] Photoionization, ref. 2. [c] ΔH_f(RCl) from ref. 5. [d] Mean value in ref. 2 is 11.37 e.v. [e] Mean value in ref. 2 is 11.19 e.v. [f] Mean value in ref. 2 is 11.83 e.v.

number, although *t*-butyl chloride shows an additional effect owing to chain branching. Heats of formation of the parent ions, $\Delta H_f(RCl^+)$, can be found by combining literature values[5] of ΔH_f(RCl) and our A.P. (RCl^+). Now it is well known that in homologous series, lengthening or branching the chain confers stability; that is, ΔH_f decreases. This is the trend found for the chloroalkane ions. Alternatively, one can regard the A.P.(RCl^+) relative to A.P.(CH_3Cl^+) as a measure of stabilization. These A.P. increments suggest that even if a localized electron on chlorine were removed in process 1, the charge on the resulting ion, $C_nH_{2n+1}Cl^+$, is then essentially delocalized as might be expected for the analogous ion, $C_nH_{2n+2}^+$.

Finally, it is usual that A.P. obtained by photoionization are lower than those found by electron impact.[2] As the reverse was found here for the chlorobutanes, this is a discrepancy which needs to be resolved.

(5) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963).

(6) National Science Foundation Senior Postdoctoral Fellow, 1963–1964. Correspondence should be addressed to the Department of Chemistry, Illinois Institute of Technology, Chicago 16, Ill.

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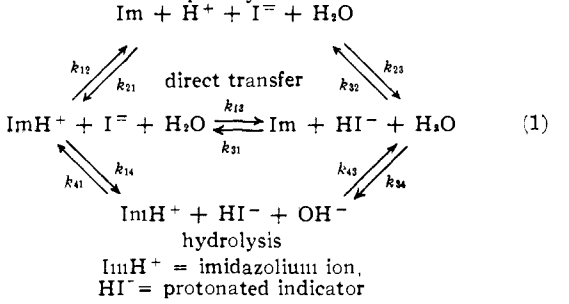
RECEIVED AUGUST 24, 1964

A Kinetic Study of the Imidazole Groups of Chymotrypsinogen, Chymotrypsin, and Some Derivatives, Using the Temperature-Jump Method

Sir:

Ionizable groups of proteins are best characterized by the rate constants of their protonic processes. It is of interest to learn through the values of these constants how the factors of protein structure modify the properties of these groups relative to those of small model compounds. Relaxation methods can provide rate constants when the protein has only a few groups of a given type. The two imidazole groups of chymotrypsin (CT) form such a case and in the presence of a pH indicator are the source of a large chemical relaxation transient measurable with a precision of 3% or better using the temperature-jump technique. The mechanism (eq. 1) is that reported for imidazole itself.[1]



(1)

The experimental data are quantitatively fit by eq. 2 and 3, derived using an appropriate steady-state treatment for $[H^+]$ and $[OH^-]$.

$$\tau^{-1} = \tau_{DT}^{-1} + \tau_P^{-1} + \tau_H^{-1} \qquad (2)$$

$$\left.\begin{aligned} \tau_{DT}^{-1} &= k_{13}(\overline{[ImH^+]} + \overline{[I^{-2}]}) + k_{31}(\overline{[Im]} + \overline{[HI^-]}) \\ \tau_P^{-1} &= \frac{k_{12}k_{23}(\overline{[ImH^+]} + \overline{[I^{-2}]}) + k_{21}k_{32}(\overline{[Im]} + \overline{[HI^-]})}{k_{23}\overline{[I^{-2}]} + k_{21}\overline{[Im]}} \\ \tau_H^{-1} &= \frac{k_{14}k_{43}(\overline{[ImH^+]} + \overline{[I^{-2}]}) + k_{41}k_{34}(\overline{[Im]} + \overline{[HI^-]})}{k_{41}\overline{[HI^-]} + k_{43}\overline{[ImH^+]}} \end{aligned}\right\} \qquad (3)$$

where τ = over-all relaxation time (10 to 70 μsec.), τ_{DT} = direct transfer relaxation time, τ_P = protolysis relaxation time, and τ_H = hydrolysis relaxation time. The bars over the concentrations indicate equilibrium concentrations at the upper temperature (10°). Our experimental system consisted of imidazole (or protein), phenol red (indicator), and 0.1 *M* KNO_3. The pH dependence of τ for imidazole and several proteins (Fig. 1) is well fitted by eq. 2 and shows a dominance of τ_{DT}. There was no complication from carboxyl or ammonium protonic processes in the pH range studied.

The dependence of τ^{-1} on total protein concentration is linear with an intercept value of $(1.00 \pm 0.05) \times 10^4$ sec.$^{-1}$ for all the proteins at pH 7.5 and 4.6×10^{-5} *M* total phenol red. According to eq. 3, the intercept is a function of all the rate constants and the indicator concentration. Although small variations in the protolytic and hydrolytic rate constants would not be detected, the constancy of the intercepts demands approximate constancy of all the rate constants or a set of accidental compensations yielding a constant intercept. Accidental compensation appears improbable and if it is rejected, k_{13}, k_{31}, k_{12}, k_{21}, k_{34}, and k_{43} are essentially invariant for all the "available" imidazole groups of chymotrypsin and its derivatives. The slope of a τ^{-1} *vs.* protein concentration plot thus measures the "available" concentration of imidazole groups, defined as those groups which are capable of reacting with indicator. The direct transfer constants k_{13} and k_{31} are then a measure of the extent to which the environment provided by the protein hinders the direct transfer reaction in eq. 1. Although the rate constants have not yet been refined with statistical methods, estimates of k_{13} and k_{31} are 2.9×10^8 and 5.8×10^7 M^{-1} sec.$^{-1}$,

(1) M. Eigen, G. G. Hammes, and K. Kustin, *J. Am. Chem. Soc.*, **82**, 3482 (1960).