$X + R \rightarrow XR$

or otherwise of the movement indicated should be obtained during the future work of the survey.

F. WILLIAMS

Inter-Territorial Marine Fisheries Research Organization,

Zanzibar.

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A Biological Agent for securing Large Numbers of Amæba proteus

THE role of Oscillatoria for purifying freshwater reservoirs is well known. For some years now, I have been applying successfully this biological agent to 'cleaning up' amœba cultures. Ordinary lab-oratory cultures, unless rigidly controlled, tend to become choked with algae in the course of time. It is a tiresome manipulation to separate out the amœbæ in sufficient numbers when it is desirable to make a quantity of stained preparations, or to secure the large numbers of young amœbæ which are required when a study of mitosis is being made. If, however, among the algal contents one introduces Oscillatoria, the filaments of this grow over and bind together the wheat grains and the algal contents into a cylindrical mass. The rest of the vesicle is quite free from weed; but young amœbæ, some rotifers and small flagellates creep out on to it and multiply, and so a white carpet is formed consisting mainly of amœbæ quite free from debris. These can then be pipetted off into the fixative, or used for a study of mitosis.

If now a new receptacle with water and wheat be prepared, the cylindrical mass can be removed bodily, placed into the prepared receptacle and squeezed, when a new culture results, which will be ready for use in about three months.

MONICA TAYLOR

Notre Dame College, Dowanhill, Glasgow.

Χ

Laws of Addition and Substitution in Atomic Reactions of Halogens

QUANTITATIVE developments of the observations communicated some time ago1 on the reaction of N-chlorosuccinimide with toluene has led to a clarification of the reaction mechanism.

Let us, however, consider first the reactions between an organic substance (RH) and a halogen (X_2) in homogeneous gaseous systems or in non-polar solutions. If the reaction proceeds by atoms and free radicals, the following reactions (substitution s, addition a) must be expected :

$$X_{\circ} + M \to 2 X + M \tag{1}$$

$$+HR \rightarrow HX + R (2s) \quad X + RH \rightarrow XRH$$
 (2a)

$$R + X_2 \rightarrow RX + X \quad (3s) \quad XRH + X_2 \rightarrow XRHX + X \quad (3a)$$

$$R + HX \rightarrow RH + X$$
 (4s) $XRH \rightarrow RH + X$ (4a)

$$\begin{array}{ccc} X + XR \rightarrow X_2 + R & (5s) & X + XRHX \rightarrow X_2 + \\ & & XRH & (5a) \end{array}$$

$$2X + M \to X_2 + M \tag{6}$$

(7s)
$$X + XRH \rightarrow XRHX$$

(or $X_2 + RH$) (7a)

$R + R \rightarrow R_2$ (8s) $XRH + XRH \rightarrow XRHRHX$ (or XRHX + RH) (8a)

By applying the usual stationary state method, the rate laws in $(X_2)^{1/2}$, (X_2) or $(X_2)^{3/2}$, which were found empirically by Bodenstein, Kistiakowsky, Schumacher, Van Artsdalen and others², are obtained. But it can be shown, in agreement with all previous observations, which of these rate laws must be expected in any specific case, by estimating the rate constants, that is, activation energies and partition functions for the eight different elementary steps. A quite satisfactory 'first approximation' is obtained in the following way : it is assumed that activation energies exceed endothermicities by 2 to 5 k.cal.; electronic and vibrational partition functions are assumed to be equal for all particles, and rotational partition functions are calculated neglecting structural particularities.

Further, the rules governing the competition of addition and substitution may be calculated; the ratio of addition to substitution being:

$$r(a/s) = k_{2a}/k_{2s}(1 + k_{4a}/k_{3a} (X_2)),$$

or for low concentrations of (X_2) —the order of magnitude of which can be estimated satisfactorily :

$$r(a/s) = k_{2a}k_{3a} (X_2)/k_{2s}k_{4a}$$

Thus addition is favoured by high, substitution by low, values of (X_2) ; this explains the 'perturbations' of addition reactions observed, for example, by Schumacher³.

It has been shown that in the reaction of Nchlorosuccinimide with toluene, traces of impurities (for example, 10^{-5} water) lead, in the course of an induction period⁴, to formation of HX, which yields with N-chlorosuccinimide halogen molecules (X_2) ; the latter give by thermal dissociation the primary halogen atoms. These could now react according to (2s) or (2a). In the first case, the following reaction chain would be started :

$$X + HR \rightarrow XH + R \qquad (a)$$

$$SNX + XH \rightarrow SNH + X_2 \qquad (b)$$

$$R + X_2 \rightarrow RX + X \qquad (c)$$

It can easily be understood that (2a) cannot be followed by a rapid reaction : (i) actually the above substitution-addition rule means that (3a) is slow as compared to (4a) so long as (X_2) is low; (ii) the alternative reaction, $SNX + XRH \rightarrow SN + XRHX$, is only possible if the dissociation energy of the SN-Xbond is smaller than or equal to an X-X bond; we have several indirect arguments for the contrary. (This reaction is certainly negligible compared with 3a because of its high (negative) entropy of activation.)

Thus the reactions (a), (b) and (c) are the only alternative. They explain all the observed facts⁴, and we believe that they can be applied also in the case of other reagents giving atomic halogenations. It is not necessary to admit *ad hoc* a 'specificity' of the SN radical, as has been done previously⁵.

Actually it appears, for the first time quantitatively, that the high specificity of reagents is due to the concentration at which reagents are maintained in a system, much more than to the inherent specificity of these reagents. We believe that this may have general importance in biological reactions. In fact,

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