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Alkyl Iodide–Iodine Exchange and the Szilard-Chalmers Effect

Abstract. *The rate of isotopic exchange between liquid ethyl iodide and dissolved iodine is of zero order with respect to iodine concentration. Apparent isotopic exchange is thus very rapid at low concentrations of iodine, and previously reported values of organic "retention," obtained in studies of* (n, γ) *recoil in alkyl iodide, are placed in doubt.*

In studies of the Szilard-Chalmers effect (*1*) several theories regarding retention of I^{128} activity in the organic phase have been proposed (*2*). Libby (*3*) has attributed retention to a cage effect on the hot atom, and Willard (*4*) has indicated that impurities in the ethyl iodide may be responsible. Shaw and Collie (*5*) found that thermal exchange occurs, but, on the basis of the work of Lind *et al.* (*6*), they assumed that ethyl iodide and iodine could not exchange activity; they further reasoned that the exchange must be between ethyl iodide and an iodine-containing intermediate such as HI:

$$C_2H_5I + HI^{128} = C_2H_5I^{128} + HI \qquad (1)$$

Reduction of the ethyl iodide-128 yield on addition of molecular iodine was attributed to the reaction:

$$HI^{128} + I-I = I-I^{128} + HI \qquad (2)$$

This theory was also consistent with Willard's because the impurity could have been the intermediate HI. In all these treatments the exchange reaction between ethyl iodide and iodine was assumed to be slow in relation to the (n, γ) process and, therefore, has not been considered in interpreting experimental data. We have found the fundamental law for rate (R) for the transfer of isotopically labeled iodine atoms between I_2 and ethyl iodide, without net chemical change,

$$C_2H_5I + I - I^{131} = C_2H_5I^{131} + I - I \quad (3)$$

to be represented experimentally by

$$R = k(C_2H_5I)^2 \qquad (4)$$

Equation 4 is valid within experimental error over a very wide range of concentrations of iodine (10^{-8} to $10^{-3}M$), from pure ethyl iodide to $3M$ solutions of ethyl iodide, at temperatures from 0° to 40°C. The value of k was found (*7*) to be $3.5 \times 10^{-9}M^{-1}$ hr^{-1} at 23°C, with a measured Arrhenius activation energy of 23 kcal/mole and an activation entropy of 40 calories per degree Celsius. This value of the rate constant was independent of exposure to air or room light; source, type, and intensity of iodine activity; presence of several common impurities; methods of purification of ethyl iodide; and oxidaton of I^- to I_2. The rate constant increased in highly polar solvents and in extensive glass surfaces. The corresponding k for the isopropyl iodide–iodine exchange system was about ten times smaller than that for ethyl iodide.

As McKay showed (*8*), the activity X of ethyl iodide is related to initial activity X_o and the activity at isotopic equilibrium, X_∞, by the molarities of the ethyl iodide and iodine pools a and b as follows:

$$\ln\left[\frac{X\infty - X_o}{X\infty - X}\right] = \left[\frac{a+b}{ab}\right] RT \quad (5)$$

For very low iodine concentrations ($b << a$) the rate law for exchange between ethyl iodide and iodine may be represented by combining Eqs. 4 and 5 and by simplifying them to

$$\ln\left[\frac{X\infty - X_o}{X\infty - X}\right] = \frac{Rt}{b} = \frac{k(C_2H_5I)^2t}{(I_2)} \quad (6)$$

Equation 6 shows that the half-time for exchange equals $0.693\ (I_2)/k(C_2H_5I)^2$. Thus the apparent or observed exchange reaction proceeds more rapidly the lower the iodine concentration, as was corroborated by experiments at $10^{-11}M$ I_2.

In Szilard-Chalmers experiments the fraction of newly formed activity retained in the target molecules is designated retention. In studies of this type on alkyl iodides the post-irradiation exchange has usually been ignored. However, any exchange that occurs before separation of the organic iodide and the recoil activity must be taken into account.

It can be seen that, even though the rate law is independent of iodine concentration, the apparent exchange (as measured by organic retention of activity) is dependent on it. At very low concentrations of iodine, apparent exchange is very fast, but, as the iodine concentration is increased, the measured apparent exchange rate falls off. If Eq. 6 were valid at extremely low concentrations of iodine, the apparent exchange rate would be too fast for measurement by standard techniques and the organic retention would be ~ 100 percent. At high concentrations of iodine the observed exchange rate becomes so slow as to require the use of very high activity levels of the isotope tracer; at such high levels the exchange induced by radiation becomes important (*9*).

The small amounts of iodine added in organic-retention studies to "carry" the activity produced in the (n,γ) reaction should also have a drastic effect on the organic retention. The half-time of the apparent exchange reaction is predicted to be 5×10^{-2} seconds in $10^{-11}M$ I_2 and 5×10^{3} seconds in $10^{-6}M$ I_2. The latter value is of the same order of magnitude as the half-life of I^{128}.

The overall effect of this exchange is to lower the organic retention at higher concentrations of iodine until none is observed to arise from the exchange reaction in the period between neutron irradiation and separation of "organic" and "inorganic" species (measurement of retention). According to Eq. 6, diluting the ethyl iodide with inert solvents will decrease the exchange rate, which will also depend on the polarity of the solvents employed; this dependency is consistent with data reported for this system (*2–5*).

The experimental technique used should also be considered because of the rapid nature of the exchange. According to these earlier arguments there should be post-irradiation exchange, as has been reported by Schuler (*10*). Thus, if solutions are not quenched or sampled immediately after bombardment, there may be a large amount of apparent exchange, depending on the concentrations of iodine and ethyl iodide.

Some thermal exchange has been observed in the methyl iodide–iodine (*11*) and is present in isopropyl iodide–iodine systems; it may also play an important role in the Szilard-Chalmers effect with these systems. It must be noted, however, that several points indicate that thermal exchange is not the sole factor in explaining organic retention in these effects: for example, lower reaction temperatures do eliminate the organic retention, and there is a finite retention at iodine concentrations at which apparent exchange should not be important. Moreover, radioactive products other than the alkyl iodide have been reported. Nevertheless, we believe that the possibility of exchange between alkyl iodide and iodine has been overlooked in these studies; thus the apparent retentions quoted in the literature are probably higher than the true retention, especially when concentrations of I_2 were very low.

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Pseudo Superglacial Till

Abstract. *A thin layer of coarse till overlies clay-rich till in northwestern North Dakota. That the thin layer is not a superglacial facies of the underlying clayey till is indicated by (i) geomorphic relations; (ii) contrasted lithologies; (iii) restricted area of exposure; (iv) absence of a similar deposit on a younger clayey till in a comparable topographic environment; (v) presence of a probable paleosol; (vi) an intervening unconformity; and (vii) occurrence of clayey facies of the upper deposit. The deposit is believed to represent a younger till.*

In northwestern North Dakota, a thin layer of silty till rests on a thick deposit of clayey till (Fig. 1). The assemblage resembles a typical complex of superglacial and lodgement tills in which the upper layer represents superglacial (and englacial) drift stranded onto a subglacial deposit during wasting of a single glacier (*1*). This early interpretation, however, encountered difficulties as the regional study progressed and it became increasingly clear that the assemblage was actually the product of two separate glaciations. In this report I describe briefly the evidence for two separate tills in the area of study and, in so doing, emphasize the need for caution in interpretation of superficially similar assemblages elsewhere.

The upper till occupies a lobate area of about 800 square miles (2100 square kilometers) in northwestern North Dakota (Fig 2). It is generally siltier than the underlying till and has a greater concentration of pebbles, cobbles, and boulders. Locally, the upper till includes thin sand seams up to 1 inch (2.5 cm) thick. Over the greater part of the area its thickness varies from a thin veneer to 15 feet (5 m) or more, and probably averages 5 feet (1.52 m). In a few places the thickness is at least 25 feet (8 m) and may be considerably more. The upper till is generally light gray in contrast to the brown till below.

The relative abundance of pebbles of the upper till, other than those of local rock types, is as follows: granitic rocks, about 32 percent; limestone and dolomite, about 44 percent; foliated metamorphic rocks, about 24 percent; and plutonic rocks other than granite, less than 1 percent. Histograms of many pebble samples (*2*) as well as till-pebble isopleth maps showing the regional variations in lithology (*3*) have been published. The source area for the erratics is in the Canadian Shield several hundred miles to the northeast.

The till is distributed over a topography of varied relief. It rests nearly everywhere on the clay-rich till, but locally overlies glaciofluvial sediments. Its surface is generally level to gently undulating, although well-developed moraines are present in several localities. The till is mantled locally by glaciofluvial deposits and regionally by loess. The loess is rarely more than 2 or 3 feet (0.6 to 1 m) thick.

Geomorphic relations in Little Muddy Valley north of Williston strongly suggest that the silty till is younger than the clayey till. The surface of the clayey till is smoothly graded and forms a terrace only lightly veneered with the silty till and loess. In many places in the terrace scarp the clayey till extends down to, and presumably below, stream level. At two localities, 12 and 18 miles (20 and 30 km) north of Williston, the silty till forms pronounced morainal topography below the level of the terrace against whose frontal scarp it abuts. The graded terrace surface could hardly have been fashioned after deposition of the silty till because the morainal topography lies at lower elevations. Nor is it likely that the terrace surface was formed while stagnant ice covered the morainal areas because the terrace is a regional phenomenon, found outside as well as inside the area of silty till. A reasonable interpretation is that the graded surface of the clayey till was subsequently trenched and that a later ice, thicker in the trenches than elsewhere, deposited the pronounced moraines.

The proportions of the erratic pebbles in the silty till differ significantly from those in the underlying clayey till. Histograms of the silty till reveal three prominent peaks representing the granitic rocks, the metamorphic foliate rocks, and limestone and dolomite. The clayey till shows a high peak for limestone and dolomite, a very small peak

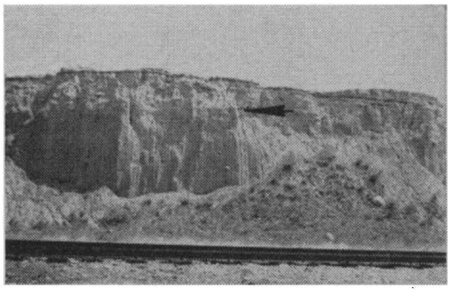

Fig. 1. Thin layer of gray, silty till overlying brown, clayey till in Jones Cut, 5 miles (8 km) southwest of Williston, North Dakota. The arrow indicates the contact. Remnants of a truncated soil are found on top of the lower till.