Radical and Polar Mechanisms for Exchange of Iodine with Organic Iodides

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In many chemical systems undergoing heterolytic substitution reactions, quantitative mechanistic study is facilitated because comparatively few independent processes take place at significant rates. By contrast, when free radicals are produced by homolytic processes, many competing reactions have very low activation energies and the kinetic interpretation becomes very complicated.

Because bonds to iodine are comparatively weak, iodine atoms discriminate among possible reactions more effectively than most other radicals do. In particular, if some molecules contain organically bound iodine, isotopically labeled iodine atoms may undergo substitution to the virtual exclusion of other processes. Hence, the isotopic exchange reactions of free iodine atoms have been particularly useful for studying effects of structure on relative rates of radical reactions.

If SI is an organic molecule containing iodine, the reaction of interest can be written

$$SI + I_2^* \longrightarrow SI^* + II^* \qquad (1)$$
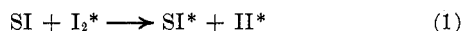
where the asterisks are used to designate atoms originally present as the free element. Because iodine-131 is an easily measured radionuclide with a half-life of 8 days, and because elementary iodine can be separated easily from most organic iodides, the reaction is very convenient for kinetic studies. The variation of exchange rate with concentration of reactants usually leads to definite mechanistic conclusions.

Reactions that proceed by free-radical mechanisms are usually clearly indicated by rates that are one-half order in iodine and by photochemical acceleration of the rate of exchange. Because absolute quantum yields for iodine dissociation and rate constants for atom recombination have been measured in several systems,[1-5] photochemical rates can be used to calculate absolute rate constants for the reactions of free iodine atoms.

As would be expected from studies of other radical reactions, most mechanisms for iodine atom exchanges either involve addition to an unsaturated system or else abstraction of a single (iodine) atom. Table I summarizes the activation energies observed for representative reaction types. As is discussed below, evidence for a direct radical substitution mechanism in saturated systems is ambiguous at best.

Table I
Activation Energies for Exchange with Iodine Atoms by Radical Mechanisms in Nonpolar Solvents

Compd	E, kcal/mole[a]	Ref
Addition Mechanisms		
trans-1,2-Diiodoethylene	8.5	6
α-Iodonaphthalene	13.3	13
β-Iodonaphthalene	14.0	13
Iodobenzene	17.2	12, 13
Allyl iodide	3.5	15
Abstraction Mechanisms		
Iodobenzene	28.4	17
Allyl iodide	8	15
Benzyl iodide	8.2	20
Methyl iodide	11.0	23
Perfluoromethyl iodide	15.8	26

[a] Most of these values are obtained by subtracting half the enthalpy of dissociation of molecular iodine from the apparent activation energy for the thermal exchange. In units of l./(mole sec), log A values for these atomic reactions usually range from 8.7 to 9.8 and are too imprecise to permit any definite correlations with structure. For methyl iodide, log A is only 7.7. Absolute atom concentrations are unknown for the photochemical experiments used to measure the temperature dependence of allyl iodide exchange.

During studies of exchange by these free-radical mechanisms, some unexpected obviously polar mechanisms were also discovered. Those reactions studied in the United States involved concentration of positive charge on the organic portion of the molecule under-

(1) J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 658 (1950).
(2) F. W. Lampe and R. M. Noyes, *J. Amer. Chem. Soc.*, **76**, 2140 (1954).
(3) H. Rosman and R. M. Noyes, *ibid.*, **80**, 2410 (1958).
(4) D. Booth and R. M. Noyes, *ibid.*, **82**, 1868 (1960).
(5) L. F. Meadows and R. M. Noyes, *ibid.*, **82**, 1872 (1960).

going exchange, and the rates were very strongly affected by changes in substituents and solvent. At about the same time, workers in Hungary discovered some reactions in which positive charge apparently concentrated on the iodine portion of the exchanging system.

Hence the isotopic exchange reactions of organic iodides with elementary iodine illustrate a remarkable variety of mechanistic types. Studies of a number of different systems have reached the point that several generalizations can be made, and it seems appropriate to discuss the factors that will cause a particular mechanism to predominate in a specified system.

Exchange by Radical Addition to Unsaturated Systems

Vinylic Iodides. Studies of vinylic iodides have concentrated on the 1,2-diiodoethylenes, CHI=CHI, so that rates of exchange could be compared with those of cis–trans isomerization. Each isomer exchanges almost stereospecifically with iodine atoms[6] with an activation energy of about 8 kcal/mole, and the rate of exchange of the somewhat more stable trans isomer can be used to monitor concentration of free iodine atoms in the system.[1,3,5,7,8] At 25°, the rate constant for this exchange in hexane is[1] 2400 l./(mole sec). Each isomer can be converted to the other with the same kinetics as for exchange and with about the same Arrhenius A factor, but the activation energy for isomerization of either isomer is about 12 kcal/mole. A potential energy diagram for these processes is shown in Figure 1.

A few mechanistic details are left ambiguous by Figure 1. Exchange of the trans isomer presumably passes through configuration I, and a rotation of 180°
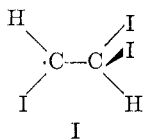
about the C–C bond would be necessary to obtain the isomeric configuration for cis exchange. It is not clear whether configuration I corresponds to transition state TX in Figure 1 or whether there is a true intermediate TI, but this configuration certainly loses an iodine atom more easily than it rotates. Since the barrier to internal rotation is about 4 kcal/mole more than the energy difference between TI and TX, and since few single bonds have rotation barriers as large as 4 kcal/mole, TI probably has little if any barrier to iodine atom dissociation. Benson, Egger, and Golden[9] estimate that TI is 6 kcal/mole unstable with respect to T + I and is hence about 2 kcal/mole more stable than TX. The radical carbon is either planar or is undergoing rapid inversion.[10]
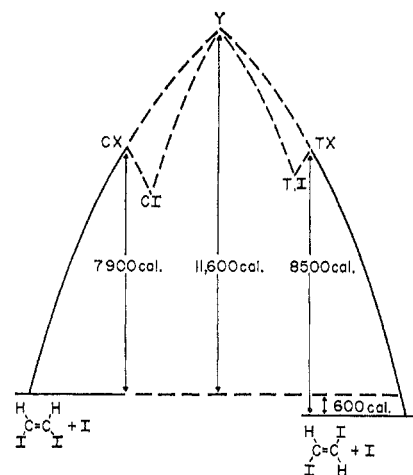

Figure 1. Energy relations in isomerization and exchange of diiodoethylene.

The kinetic data do not determine whether the entering iodine atom adds directly to one of the two carbons or whether it first interacts with the π electrons of the double bond to form a metastable bridged radical having less energy than TX. The question could be answered in principle by studies of the analogous bromine system. If cis–trans isomerism is neglected, the reactions in this system are

$$C_2H_2Br_2 + Br \rightleftharpoons C_2H_2Br_3 \qquad (2)$$

$$C_2H_2Br_3 + Br_2 \longrightarrow C_2H_2Br_4 + Br \qquad (3)$$
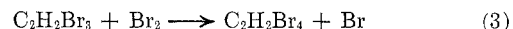
If bromine concentration is low, reaction 2 is reversible and has virtually no activation energy in the forward direction.[11] The three transition states in the bromine system equivalent to TX, CX, and Y in Figure 1 have identical energies within 1 kcal/mole. If the bromine concentration were sufficiently great, reaction 2 could be made rate determining for the bromination process and its rate constant could be measured. If the entering bromine atom added specifically to one carbon atom, the rate constant for exchange at low bromine concentrations would be 0.50 of the rate constant for step 2 of bromination. If the entering bromine atom added to the double bond and scrambled all three bromines before it dissociated, the rate constant for exchange would be 0.67 of that for bromination. The difficult experiments to distinguish these alternatives have not yet been attempted.

Aromatic Iodides. Conjugated aromatic systems can also add radical agents, and iodobenzene could be expected to exchange with iodine atoms by passing through an intermediate or transition state like configuration II in which the odd electron is delocalized. Independent studies indicated 15.9[12] and 18.5[13] kcal/mole for exchange of iodine atoms with iodobenzene in

(6) R. M. Noyes, R. G. Dickinson, and V. Schomaker, *J. Amer. Chem. Soc.*, **67**, 1319 (1945).

(7) G. A. Salmon and R. M. Noyes, *ibid.*, **84**, 672 (1962).

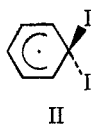(8) S. A. Levison and R. M. Noyes, *ibid.*, **86**, 4525 (1964).

(9) S. W. Benson, K. W. Egger, and D. M. Golden, *ibid.*, **87**, 468 (1965).

(10) R. M. Noyes, D. E. Applequist, S. W. Benson, D. M. Golden, and P. S. Skell, *J. Chem. Phys.*, **46**, 1221 (1967).

(11) H. Steinmetz and R. M. Noyes, *J. Amer. Chem. Soc.*, **74**, 4141 (1952).

(12) S. Levine and R. M. Noyes, *ibid.*, **80**, 2401 (1958).

(13) M. Nakashima, C. Y. Mok, and R. M. Noyes, *ibid.*, **91**, 7635 (1969).

II

perchlorobutadiene solvent; these values are about twice the 8 kcal/mole for exchange of the olefinic diiodoethylene. Rates of exchange of aromatic iodides differ by rather small factors between perchlorobutadiene and nitrobenzene even though the room temperature dielectric constants of these solvents are 2.6 and 35, respectively; hence the transition states differ little in polarity from the compounds themselves. Although the exchange reaction undoubtedly passes through a σ-complex structure like configuration II, the kinetic data say nothing about the possible intervention of π-complex intermediates.

Quantitative comparison of different compounds is rendered somewhat difficult by catalytic effects apparently associated with methods of cleaning the glass reaction vessels. These effects were responsible for initial claims[12] of a polar mechanism of exchange for iodobenzene, but the radical mechanism seems now[13] to have been isolated unambiguously. Extrapolation of rates to 160° indicates a 10^5-fold range between diiodoethylene and iodobenzene, with the iodonaphthalenes behaving intermediately.[13] The data correlated fairly well with Hückel localization energies, but the limited data on substituted iodobenzenes correlated poorly with the Hammett equation.[14] Thus, the rate of exchange of iodobenzene is accelerated about a factor of ten by a p-methoxy substituent and decelerated only slightly by a p-nitro group. Iodine atoms evidently behave as electrophilic agents toward aromatic systems, but the relative rates do not seem to correlate well with parameters developed for other types of reactions. There have been rather few quantitative kinetic studies of direct addition of radicals to aromatic systems, and these exchanges seem well suited to a thorough study.

Allylic Iodides. In vinylic and aromatic iodides, the iodine is attached to an sp²-hybridized carbon that is involved in π bonding; exchange involves iodine atom addition to form a σ-complex intermediate or transition state. The iodine in allyl iodide is attached to an sp³-hybridized carbon. However, allyl iodide undergoes a dramatically rapid exchange with iodine atoms. In hexane at 25°, the rate constant is 5×10^6 l./(mole sec)[15] or about 2000 times as great as that for trans-diiodoethylene! If the molecule is labeled with carbon-14, iodine atoms cause a scrambling of the two end carbons at a rate about 50% that of the iodine exchange.[16] Hence the end carbons are almost but not quite equivalent in structure at the time the entering and leaving iodines have become equivalent. The rate of exchange is about 2000 times as great as that at which free allyl radicals are produced in the same system.[2,15]

Any explanation of this amazingly facile reaction must invoke some unconventional radical structures. The activation energy of only about 3.5 kcal/mole makes it doubtful that an iodine atom adds to form a σ-complex type of intermediate, and the lack of equality of rates of carbon scrambling and iodine exchange rules out a transition state of form $I \cdots CH_2 \overset{..}{-} CH \overset{..}{-} CH_2 \cdots I$. The data are consistent with a transition state like configuration III in which iodine atoms on opposite sides of the plane of the carbons interact with the π-

III
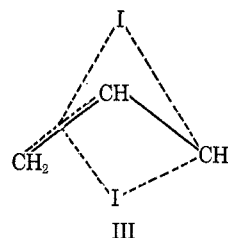
electron clouds of a still unsymmetrical allyl radical. However, the experimental facts must be allowed to stand by themselves without any unequivocal mechanistic interpretation.

Exchange by Radical Abstraction of Iodine

General Considerations. An iodine atom can always in principle abstract an iodine from SI according to eq 4. The reaction as written is almost always endother-

$$SI + I \cdot \longrightarrow S \cdot + I_2 \qquad (4)$$
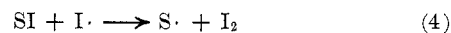
mic, and the reverse reaction to form SI is probably virtually diffusion controlled. If molecular iodine is the most effective radical scavenger in the system, step 4 is then rate determining for an atom-initiated isotopic exchange. If other radical scavengers such as molecular oxygen are also present, step 4 can serve to initiate decomposition of SI rather than isotopic exchange.

The strength of the I–I bond is close to 35.6 kcal/mole in most solvents, and the activation energy for exchange by this mechanism is related simply to the strength of the C–I bond in SI.

Vinylic Iodides. By comparison with effects of changing structure on the strengths of other bonds, the C–I bond in vinyl iodide is estimated to be about 60 kcal/mole. Hence the activation energy should be about 24 kcal/mole for exchange of vinylic iodides by abstraction. As discussed above, exchange by the addition mechanism has an activation energy of only about 8 kcal/mole and obviously predominates. Iodine atoms do not initiate significant decomposition of diiodoethylene even if air is present in the system.

Aromatic Iodides. Rodgers, Golden, and Benson[17] report a gas-phase activation energy of 28.4 kcal/mole for abstraction from iodobenzene by step 4. As indicated above, the observed[12,13] activation energy of about 17 kcal/mole for exchange supports the σ-complex mechanism without significant contribution from abstraction. This conclusion is supported by the observation that the rates of exchange are not detectably different in degassed and in air-saturated solutions.

(14) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940, p 186.

(15) D. J. Sibbett and R. M. Noyes, J. Amer. Chem. Soc., **75**, 763 (1953).

(16) W. P. Cain and R. M. Noyes, ibid., **81**, 2031 (1959).

(17) A. S. Rodgers, D. M. Golden, and S. W. Benson, ibid., **89**, 4578 (1967).

Allylic Iodides. As discussed above, direct exchange of allyl iodide with iodine atoms is about 3000 times as fast as is abstraction by step 4.[2,15] The abstraction from allyl iodide is about the same rate as the exchange of *trans*-diiodoethylene, which has an activation energy of about 8 kcal/mole. This is just the activation energy expected for abstraction from allyl iodide with a C–I bond energy[18] of 43.5 kcal/mole.

Benzylic Iodides. Benzyl iodide exchanges with iodine atoms with a rate constant about 3×10^4 l./(mole sec) in dichloroethane at 30°.[19] This rate is actually somewhat *slower* than would be expected for the abstraction mechanism if the bond energy is as low as 40 kcal/mole.[18] Free benzyl radicals are clearly present as intermediates,[20] and the rate of exchange is inhibited by oxygen. However, extrapolations suggest that about one-third of the exchanges could not be prevented by oxygen.[19]

A *p*-nitro substituent accelerates the reaction and a *p*-methyl decelerates it,[19] corresponding to a Hammett[14] ρ of about 1.0. Since such substituents have opposite effects on rates of radical abstraction of benzylic hydrogen,[21,22] directions of substituent effects obviously depend upon the polarity of bonds even during homolytic cleavage.

Primary and Secondary Alkyl Iodides. Alkyl iodides could not exchange with iodine atoms by an addition mechanism but could exchange by the abstraction mechanism of step 4. In perchlorobutadiene solvent at about 160°, primary and secondary iodides do apparently exchange by radical mechanisms. Relative rates of exchange of primary iodides fit the sequence[23,24] $CH_3I < CH_3CH_2I < CH_3CH_2CH_2I \approx (CH_3)_2CHCH_2I \gg (CH_3)_3CCH_2I$. The secondary iodides $(CH_3)_2CHI$ and $CH_3CH_2CHICH_3$ each exchange at about the same rate but faster than any primary iodide.[23,25] Exchange is usually slower in air-saturated than in degassed solutions, but the effect is seldom more than about a factor of two.[23] Abstraction of β hydrogen by eq 5 is possible

$$RR'CHCHIR'' + I\cdot \longrightarrow RR'C{=}CHR'' + HI + I\cdot \quad (5)$$
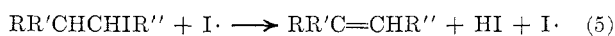
except for the slowly reacting methyl and neopentyl iodides, and it is a major reaction with isobutyl iodide;[24] however, it does not apparently contribute directly to the rate of exchange. Observed activation energies are usually at least 5 kcal/mole too low to explain the data by invoking the abstraction mechanism with accepted bond energies,[18] but the footnote to Table I indicates

that the preexponential factors for these reactions are at least a factor of ten smaller than for the other atomic exchange reactions. As was pointed out in the introduction, chemical systems are apt to become too complicated for detailed kinetic analysis whenever free radicals other than iodine atoms are produced in significant yield; the primary and secondary alkyl iodide exchanges serve to reinforce that conclusion!

Perfluoroalkyl Iodides. The exchange reactions of gaseous CF_3I[26] and C_2F_5I[27] have been studied by Laurence. The reactions are free radical and apparently proceed by the abstraction of step 4. They are less subject to heterogeneous effects than are reactions of the corresponding alkyl iodides. No attempt has been made to study exchange of perfluoroalkyl iodides in polar solvents, and mechanisms involving positive iodine might well be observed in such cases.

Possibilities of Radical Exchange by Direct Substitution

Another conceivable mechanism for radical exchange by alkyl iodides is direct substitution according to eq 6. If such a reaction went with inversion on car-

$$SI + I^* \longrightarrow SI^* + I \quad (6)$$
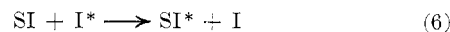
bon, the rate constant for racemization of optically active SI would be twice the rate constant for exchange. If exchange were initiated by abstraction step 4 followed by reaction of the resulting racemic radical, the rate constants for racemization and exchange would be equal.

Studies with optically active *sec*-butyl iodide in perchlorobutadiene solvent[25] indicate that racemization is about 1.5 times as fast as exchange. This result suggests that steps 4 and 6 proceed at about equal rates for this molecule. However, it should be noted that step 4 first produces a geminate pair[28] consisting of a radical and an iodine molecule. If the racemic radical were to react with the *identical* iodine molecule, only half such events would result in exchange and the rate constant for racemization would be twice that for exchange. Hence the *sec*-butyl iodide[25] results could be interpreted to indicate that half the radicals produced react with geminate iodine molecules.

It is interesting to note that oxygen can inhibit only about half the exchange observed in degassed solutions of primary,[23] secondary,[23,25] and benzyl[19] iodides. It would be extremely fortuitous if steps 4 and 6 went at almost equal rates for each of these structurally different compounds, and it seems more plausible to postulate that all radicals have about equal efficiency for geminate reaction with iodine molecules. Unless the *sec*-butyl iodide results can be repeated in an indubitably homogeneous gas-phase system, the case for step 6 must be considered unproven.

(18) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 215.

(19) I. J. Gardner and R. M. Noyes, *J. Amer. Chem. Soc.*, **83**, 2409 (1961).

(20) M. Gazith and R. M. Noyes, *ibid.*, **77**, 6091 (1955).

(21) E. C. Kooyman, R. van Helden, and A. F. Bickel, *Proc. Kon. Ned. Akad. Wetensch.*, Ser. B, **56**, 75 (1953).

(22) K. M. Johnston and G. H. Williams, *J. Chem. Soc.*, 1446 (1960).

(23) J. E. Bujake, Jr., M. W. T. Pratt, and R. M. Noyes, *J. Amer. Chem. Soc.*, **83**, 1547 (1961).

(24) M. Nakashima and R. M. Noyes, *Int. J. Chem. Kinet.*, **1**, 391 (1969).

(25) R. A. Herrmann and R. M. Noyes, *J. Amer. Chem. Soc.*, **78**, 5764 (1956).

(26) G. S. Laurence, *Trans. Faraday Soc.*, **63**, 1155 (1967).

(27) C. Grygorcewicz and G. S. Laurence, *J. Phys. Chem.*, **72**, 1811 (1968).

(28) R. M. Noyes, *J. Amer. Chem. Soc.*, **77**, 2042 (1955).

Exchange by Polar Mechanisms Involving Negative Iodine

Tertiary and Secondary Alkyl Iodides. All of the free-radical mechanisms discussed above are initiated by free iodine atoms. *tert*-Butyl iodide exchanges by an entirely different mechanism.[29] Light intense enough to change the free atom concentration by several orders of magnitude has virtually no effect on the rate of exchange. The rate is more than first order in *molecular* iodine and is unaffected if air is swept out with oxygen or nitrogen. The temperature dependence is low, corresponding to an activation energy less than half the enthalpy of dissociation of iodine, and the entropy of activation is very negative. Cooling to a temperature at which iodine would precipitate induces complete exchange. The rate is very dependent upon polarity of solvent, being over 100 times more rapid in 1,2-dichloroethane (dielectric constant 10.1) than it is in hexane (dielectric constant 1.9).

These observations indicate a very polar exchange mechanism with considerable charge separation in the transition state. The kinetics for compounds that have been studied to date can be fitted empirically to the form

$$v = k_0[\text{SI}] + k_1[\text{SI}][\text{I}_2] + k_2[\text{SI}][\text{I}_2]^2 + k_3[\text{SI}][\text{I}_2]^3 \tag{7}$$

where v is the rate of exchange of SI and two terms are usually sufficient to fit the data over a considerable range of iodine concentrations. Activation parameters (with standard states in moles/liter) for the various polar exchanges that have been studied to date are presented in Table II.

It is proposed that the transition state resembles an ion-pair-like configuration, IV ($\text{S}^+\text{I}_3{}^-$), in which the positively charged organic group is moving from one end to the other of the $\text{I}_3{}^-$ ion. Additional stabilization may be provided by other molecules of iodine that interact by polarization forces with one or the other charged portion of configuration IV. The species $\text{I}_3{}^-$ is well known in aqueous solution, and Parker[30] has shown that just such a large polarizable species is the most favored type of anion in aprotic solvents. Contribution of this mechanism to exchange of any specific SI will depend strongly upon the extent to which positive charge on S^+ can be dispersed by resonance and other interactions.

The importance of structure is illustrated by the observation that *tert*-butyl iodide in perchlorocarbon solvents exchanges readily by the polar mechanism at room temperature and below[29] while isopropyl iodide in the same solvents exchanges slowly by the radical abstraction mechanism at temperatures above 130°.[23] However, isopropyl iodide exchanges by the polar mechanism in aprotic solvents with permanent dipoles like nitrobenzene and propylene carbonate.[31] In 1,2-dichloroethane as solvent, *tert*-butyl iodide exchanges almost too rapidly to measure at 25°, while isopropyl iodide exchanges almost too slowly to study easily at 90°. However, it appears that one or the other of these two iodides will exchange at a measurable rate in any aprotic solvent from saturated hydrocarbons to solvents with very high dielectric constants. These reactions should therefore be very useful to study abilities of solvents to support formation of very polar transition states. Such studies should supplement similar ones on the very polar reaction of amine quaternization.[32]

Benzoyl Iodides. Benzoyl iodide exchanges with iodine by the polar mechanism discussed above.[33] *p*-Chloro and *p*-nitro substituents slow the rate,[34] as would be expected if the iodine part of the transition state were negatively charged. Especially in hexane solvent, the magnitudes of substituent effects are very large, as would be expected for a very polar transition state in a solvent of very low dielectric constant, but the data are rather poorly consistent with the Hammett[14] equation. It is conceivable that the strongly electron-withdrawing nitro group promotes a transition state with positively charged iodine fragments, as suggested by the examples below.

Benzhydryl Iodides. Benzhydryl iodide, $(\text{C}_6\text{H}_5)_2\text{CHI}$, also exchanges by the polar mechanism at ambient temperatures in solvents of very low dielectric constant,[35] and substituents in the aromatic ring greatly affect the rate.[35,36] Although these compounds do not exhibit the anomalous k_0 contribution to the rate that is observed with the benzoyl iodides, it is impossible to study effects of strongly electron-withdrawing substituents because these benzhydryl iodides are very sensitive to decomposition by radical mechanisms.[36]

Allyl Iodide. Allyl iodide was the first compound observed to exchange by a polar mechanism,[37] although the mechanistic implications were not realized at the time. The entropy of activation is somewhat less negative than for the other polar exchange reactions, indicating less charge separation. About 80% of exchanges result in iodine bound to the same carbon to which it was originally attached,[16] but a significant fraction of exchange is accompanied by scrambling of the end carbon atoms. In the $\text{C}_3\text{H}_5{}^+\text{I}_3{}^-$ intermediate, the end iodines apparently interchange somewhat more easily than the end carbons.

Other Compounds. When solutions of iodine and *p*-iodoanisole (*p*-methoxyiodobenzene) in perchlorobutadiene are cooled to Dry Ice temperature, some exchange is induced.[13] This compound is the aromatic

(29) J. E. Bujake, Jr., and R. M. Noyes, *J. Amer. Chem. Soc.*, **83**, 1555 (1961).

(30) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

(31) S. G. S. Stafford, unpublished observations.

(32) C. Lassau and J. C. Jungers, *Bull. Soc. Chim. Fr.*, 2678 (1968).

(33) A. Goldman and R. M. Noyes, *J. Amer. Chem. Soc.*, **79**, 5370 (1957).

(34) D. W. Hamilton and R. M. Noyes, *ibid.*, **91**, 1740 (1969).

(35) W. J. Muizebelt and R. M. Noyes, *ibid.*, **92**, 6012 (1970).

(36) J. A. Hemmingson, unpublished observations.

(37) D. J. Sibbett and R. M. Noyes, *J. Amer. Chem. Soc.*, **75**, 761 (1953).

Table II
Activation Parameters for Iodine Exchange by Polar Mechanisms

| Compd	Solvent	Temp range, °C	E, kcal/mole				ΔS‡, eu				Ref
			k_0	k_1	k_2	k_3	k_0	k_1	k_2	k_3	
(CH₃)₂CHI	C₃H₆CO₃^a	40–65			17.6				−17		31
	C₆H₅NO₂	65–90		20.0	15.3			−21	−28		31
(CH₃)₃CI	C₄Cl₆	25–60			10.8				−33		29
	C₂H₄Cl₂	0–25		9.7	11.4			−44	−20		29
CH₂=CHCH₂I	C₆H₁₄	0–40		13.1				−27			37
CH₃COCH₂I	C₆H₆	30–58	17.8				−28				49
	C₂H₄Cl₂	25–50		3.0	6.6			−58	−38		51
CH₂ICOOH	C₆H₆	35–60	14.0				−31				50
C₆H₅COI	C₆H₁₄	0–40		5.1	1.9			−53	−55		33
p-ClC₆H₄COI	C₆H₁₄	25–60		15.9	7.2			−24	−41		34
	C₂H₄Cl₂	0–40	7.7	11.5	3.3		−56	−25	−44		34
p-NO₂C₆H₄COI	C₆H₁₄	40–60	9.9	14.2			−57	−33			34
	C₂H₄Cl₂	0–40	14.8	25.4			−34	+9			34
C₆H₅CHIC₆H₅	C₆H₁₄	0–40		11.0	1.3			−32	−47		35
	CCl₄	0–25		10.0	3.0			−27	−38		35
p-ClC₆H₄CHIC₆H₅	C₆H₁₄	0–40		10.0	2.6			−36	−43		35
	CCl₄	0–40		11.3	4.1			−27	−36		35
m-ClC₆H₄CHIC₆H₅	C₂H₄Cl₂	0–25		9.4	7.7			−25	−19		35
IAp	CS₂	3–25			−6.4	−6.9			−82	−71	39
	C₂H₄Cl₂	0–35			−3.1	−2.5			−41	−34	47
	C₆H₆	10–40			0.0	0.0			−60	−49	39
	C₂H₅OH	20–40			7.8	7.4			−31	−25	39
IMepyr	CHCl₃	0–35			3.8	−5.5			−43	−62	40
	C₂H₅OH	0–35			6.3				−29		40
IPyr	C₂H₄Cl₂	10–30		12.2				−23			47
	C₆H₆	10–30		6.2				−37			47
IAcpyr	C₂H₄Cl₂	20–40	9.2				−51				47
	C₆H₆	10–30	21.0				−9				47

^{a} Propylene carbonate.

iodide that can most easily exchange by a polar mechanism, but at any temperature where the rate of homogeneous exchange could be followed the kinetics indicated that the free-radical mechanism had become dominant. Runs extended for very long times at lower temperatures might reveal a contribution from the polar mechanism.

Although all of our studies of benzyl iodides revealed only free-radical mechanisms,[19,20] polar mechanisms could undoubtedly be observed in aprotic solvents of high dielectric constant such as those giving polar exchange of isopropyl iodide.

Exchange by Polar Mechanisms Involving Positive Iodine

While the polar exchange reactions of the preceding section were being studied in the United States, workers in Budapest were examining some other highly polar exchanges. The principal iodine-containing compounds studied were the substituted iodopyrazolin-5-ones

IAp, X = I; R = C₆H₅
IMepyr, X = I; R = CH₃
IAcpyr, X = COCH₂I; R = C₆H₅

IPyr
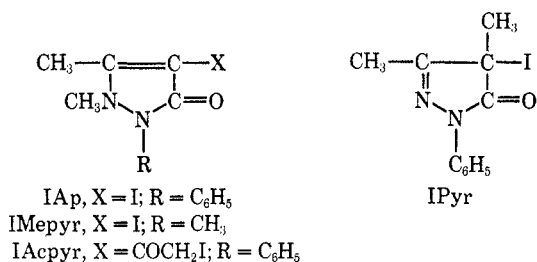
For the organic iodides discussed in the preceding section, heterolytic dissociation would be expected to yield a negative iodide ion and a positively charged organic fragment. Exactly the opposite behavior is indicated for the 4-iodopyrazolin-5-ones (IAp, IMepyr, and IPyr) that have been studied. Thus, reagents like ICl or HOI are used to replace hydrogen with iodine in the synthesis of these compounds, and the compounds themselves react with acidified iodide solutions to form elementary iodine.

Exchange of 4-Iodo-3-pyrazolin-5-ones. Rates of exchange in a number of solvents have been studied for 1-phenyl-2,3-dimethyl-4-iodo-3-pyrazolin-5-one (IAp)[38,39] and for 1,2,3-trimethyl-4-iodo-3-pyrazolin-5-one (IMepyr).[40] The data fit eq 8. Rates of exchange

$$v = k_2[\text{SI}][\text{I}_2]^2 + k_3[\text{SI}][\text{I}_2]^3 \qquad (8)$$

are not significantly affected by light or by oxygen, but the rate is greatly increased as the dielectric constant is increased by nitrobenzene addition.[41] Entropies of activation are very negative, and activation energies are low or even negative in some solvents of low polarity. Methyl- (IMepyr) and phenyl- (IAp) substituted compounds exchange at very similar rates.

(38) E. Körös, L. Pataki, L. Ladányi, and M. Orbán, *Magy. Kem. Foly.*, **72**, 130 (1966).
(39) E. Körös and M. Orbán, *ibid.*, **73**, 261 (1967).
(40) E. Körös, M. Orbán, and A. Meszticzky, *ibid.*, **73**, 463 (1967).
(41) E. Körös, M. Orbán, L. Ladányi, and L. Pataki, *ibid.*, **71**, 463 (1965).

The term in $[I_2]^3$ becomes less important in solvents that tend to complex molecular iodine. Low concentrations of electrophilic species that interact strongly with iodide ion, such as Hg(II) and Ag(I), greatly accelerate the exchange and make it virtually instantaneous.[42] On the other hand, pyridine and its derivatives reduce the rate, particularly in solvents that do not coordinate iodine well.[43] These compounds do not exchange at a significant rate with iodide ion.[44]

Kinetic measurements can determine the empirical formula of a transition state but neither its structure nor the order in which the iodine molecules are introduced.[45] Both of these compounds have a carbon–carbon double bond adjacent to the iodine, and evidence from infrared and magnetic resonance measurements indicates that molecular iodine forms a π complex with the pyrazoline.[46] Presumably polarization of the double bond facilitates an exchange that involves at least one other iodine molecule and that places partial positive charge on the iodine undergoing exchange.

Exchange of a 4-Iodo-2-pyrazolin-5-one. Somewhat different exchange behavior is exhibited by 1-phenyl-3,4-dimethyl-4-iodo-2-pyrazolin-5-one (IPyr).[47] This compound has a methyl group on the carbon containing iodine, and there is no multiple bonding to that carbon. The rate of exchange can be fitted to eq 9. This com-

$$v = k_1[\text{IPyr}][I_2] \tag{9}$$

pound also does not exchange with iodide ion.

Presumably the transition state for IPyr exchange contains fewer iodine molecules than those for IAp and IMepyr because there is no double bond adjacent to the reaction center and perhaps also because of steric effects associated with the adjacent methyl group.[48] The iodine undergoing exchange presumably bears partial positive charge.

Exchange of Iodomethylcarbonyl Compounds. Iodoacetone,[49] iodoacetic acid,[50] and IAcpyr[47] all contain a $COCH_2I$ grouping. Rates of exchange of all three compounds have been studied in benzene solvent and found to obey expression 10. Preexponential factors indicate

$$v = k_0[\text{SI}] \tag{10}$$

very negative entropies of activation, suggesting a very

polar transition state, but the rate of exchange of IAcpyr in dichloroethane is actually less than that in benzene, in opposition to what would be expected for considerable charge separation. Wong and Noyes[51] studied the exchange of iodoacetone in hexane and in dichloroethane and obtained rather unsatisfactory kinetics. However, the exchange rates they found in this solvent depended much more on iodine concentration than did the rates found by Körös, Orbán, and Füssy[49] for exchange of the same compound in benzene.

The mechanism of these exchanges is obscure. Although the rate-determining step might be a unimolecular rearrangement such as $RCOCH_2I \rightarrow RC(OI)\!=\!CH_2$, the very negative apparent entropies of activation are difficult to reconcile with the rather small rate effects of changing solvent.

Conclusions

The exchange reactions discussed above exhibit a remarkable range of mechanisms considering that all processes involve the same diatomic element and lead to no net chemical change in the system being studied!

The processes involving free iodine atoms generally resemble mechanistic types observed for reactions of other free radicals. However, the remarkably facile exchange of allyl iodide with iodine atoms is unprecedented, and some of the other exchanges exhibit unusual reversible features because addition of an iodine atom to a π-electron system is an endothermic process.

The polar exchanges involving iodine molecules are less conventional. Although a single atom of iodine is exchanged from the organic molecule, the kinetics indicate that several molecules of iodine participate in forming the transition state. The rates of many iodine additions to unsaturated molecules are also much more than first order in molecular iodine.[52] An extreme example of this effect is the observation that many of our solutions undergo complete isotopic exchange if they are cooled to Dry Ice temperature and rewarmed. Apparently even at this low temperature the iodine crystals are such efficient catalysts that exchange takes place on the surface faster than the deposition or solution of iodine molecules. Whenever several iodine molecules are present simultaneously in the transition state, the process is apparently accompanied by considerable separation of charge, and the extreme polarizability of iodine is undoubtedly involved in its ability to promote these unusual reactions.

(42) E. Körös, E. Schulek, and L. Pataki, *J. Inorg. Nucl. Chem.*, **15**, 188 (1960).
(43) E. Körös, L. Pataki, L. Ladányi, M. Orbán, and V. Keresztes-Hamer, *Acta Chim. Hung.*, **41**, 171 (1964).
(44) E. Körös, L. Pataki, and E. Schulek, Proceedings of the Conference on Radioisotopes in Physical Sciences and Industry, IAEA, Vienna, 1962, p 315.
(45) E. Körös, *Allg. Prakt. Chem.*, **20**, 32 (1969).
(46) E. Körös, unpublished observations.
(47) E. Körös, M. Orbán, M. Burger, and K. Vörös, *Magy. Kem. Foly.*, **75**, 499 (1969).
(48) E. Körös and M. Orbán, *Radiochem. Radioanal. Lett.*, **1**, 87 (1969).
(49) E. Körös, M. Orbán, and E. Füssy, *ibid.*, **1**, 203 (1969).
(50) E. Körös, M. Orbán, and M. Burger, *ibid.*, **4**, 165 (1970).
(51) S.-W. Wong and R. M. Noyes, *J. Amer. Chem. Soc.*, **86**, 3787 (1964).
(52) E. Körös, *Acta Chim. Hung.*, **67**, 195 (1971).