

Table I. Rate Constants of Charge Transfer in the Exothermic Direction in Charge-Transfer Equilibria

	cm ³ /molecule s × 10 ¹⁰			T, °C	Ref
	K _{eq}	k _f	Z _f ^a		
NO ⁺ + C ₆ D ₆ ⇌ C ₆ D ₆ ⁺ + NO	119.0	14.3	16.0	350	This work ^b
C ₆ H ₆ ⁺ + C ₆ H ₅ Cl ⇌ C ₆ H ₅ Cl ⁺ + C ₆ H ₆	28	17	15	410	3d
c-C ₄ H ₄ O ⁺ + C ₆ H ₅ CH ₃ ⇌ C ₆ H ₅ CH ₃ ⁺ + C ₄ H ₄ O	12.6	12.8	13.2	350	This work ^b
C ₆ H ₅ CH ₃ ⁺ + C ₆ H ₅ C ₂ H ₅ ⇌ C ₆ H ₅ C ₂ H ₅ ⁺ + C ₆ H ₅ CH ₃	5.3	12.8	12.6	350	This work ^b
C ₆ H ₅ CF ₃ ⁺ + C ₆ F ₅ H ⇌ C ₆ F ₅ H ⁺ + C ₆ H ₅ CF ₃	3.5	11.6	11.1	350	This work ^b
C ₆ H ₅ F ⁺ + p-C ₆ H ₄ F ₂ ⇌ C ₆ H ₄ F ₂ ⁺ + C ₆ H ₅ F	3.5	10.2	10.4	350	This work ^b

^a Calculated from equations listed in ref 6. Values of α and μ_D taken from ref 8. ^b Determined in the NBS pulsed ICR mass spectrometer using the double-resonance ion-ejection technique. Accuracy: $\pm 15\%$.

Table II. Rate Constants of Charge Transfer in the Endothermic Direction in Charge-Transfer Equilibria

	cm ³ /molecule s × 10 ¹⁰			kcal/mol ^a	
	k _r ^b	Z _r ^c	k _r ≡ Z _r e ^{-ΔH(Lit.)/RT}	ΔH = RT ln(k _r /Z _r)	ΔH, lit. ^d
c-C ₄ H ₄ O ⁺ + C ₆ H ₅ CH ₃ ⇌ C ₆ H ₅ CH ₃ ⁺ + c-C ₄ H ₄ O	1.0	9.8	0.9	-1.4	-1.4
C ₆ H ₅ F ⁺ + p-C ₆ H ₄ F ₂ ⇌ p-C ₆ H ₄ F ₂ ⁺ + C ₆ H ₅ F	2.4	13.6	2.0	-1.0	-1.1
1,2,4,5-C ₆ H ₂ F ₄ ⁺ + NO ⇌ NO ⁺ + 1,2,4,5-C ₆ H ₂ F ₄	1.3	15.0	1.2	-1.5	-1.5
C ₆ H ₅ CH ₃ ⁺ + C ₆ H ₅ C ₂ H ₅ ⇌ C ₆ H ₅ C ₂ H ₅ ⁺ + C ₆ H ₅ CH ₃	2.0	11.8	1.7	-1.1	-1.1
C ₆ H ₅ CH ₃ ⁺ + 4-FC ₆ H ₄ CH ₃ ⇌ 4-FC ₆ H ₄ CH ₃ ⁺ + C ₆ H ₅ CH ₃	2.8	11.7	3.0	-0.86	-0.81

^a 1 kcal/mol = 4.18 kJ = 0.043 eV. ^b Determined in the NBS pulsed ICR mass spectrometer using the double-resonance ion-ejection technique. Accuracy: $\pm 15\%$. ^c Calculated from equations listed in ref 6. Values of α and μ_D taken from ref 8. ^d Reference 9.

Table III. Comparison of Experimentally Determined Entropy Changes with Those Calculated from $\Delta S_{\text{coll}} = R \ln(Z_f/Z_r)$

	ΔS _{exp} , eu	ΔS _{coll} , ^a eu	Ref
C ₆ H ₅ Br ⁺ + C ₆ H ₅ I ⇌ C ₆ H ₅ I ⁺ + C ₆ H ₅ Br	-0.7	0.0	3d
C ₆ H ₅ Br ⁺ + C ₆ H ₅ CH ₃ ⇌ C ₆ H ₅ CH ₃ ⁺ + C ₆ H ₅ Br	-2	-0.5	3d
C ₆ H ₅ CH ₃ ⁺ + 1,2-C ₆ H ₄ (CH ₃) ₂ ⇌ 1,2-C ₆ H ₄ (CH ₃) ₃ ⁺ + C ₆ H ₅ CH ₃	+2	+0.2	3d
1,2-C ₆ H ₄ (CH ₃) ₂ + C ₆ H ₅ OCH ₃ ⇌ C ₆ H ₅ OCH ₃ ⁺ + 1,2-C ₆ H ₄ (CH ₃) ₂	+2	+0.2	3d
1,3,5-C ₆ H ₃ (CH ₃) ₃ ⁺ + C ₆ H ₅ OCH ₃ ⇌ C ₆ H ₅ OCH ₃ ⁺ + 1,3,5-C ₆ H ₃ (CH ₃) ₃	+2	+0.2	3d
CS ₂ ⁺ + C ₆ H ₅ CN ⇌ C ₆ H ₅ CN ⁺ + CS ₂	+2	+2.0	3d
H ₃ O ⁺ + H ₂ S ⇌ H ₃ S ⁺ + H ₂ O	-1.0 ± 0.4	-0.4	2a
C ₂ H ₅ OH ₂ ⁺ + HCO ₂ CH ₃ ⇌ H ₂ CO ₂ CH ₃ ⁺ + C ₂ H ₅ OH	+0.1 ± 0.4	+0.1	2a

^a Calcd: $\Delta S_{\text{coll}} = R \ln(Z_f/Z_r)$. Z_f and Z_r were calculated using equations listed in ref 6. Values of α and μ_D taken from ref 8.

intermolecular interactions can be estimated from the ratio of the ion-molecule collision rates in the forward and reverse directions. This contribution is small (≤ 3 eu), but is usually ignored and often results in a net change in the calculated enthalpy which is greater than the claimed accuracy.

The existence of such a term in the entropy is inevitable if one expresses the forward and reverse rate constants in terms of collision theory, as is noted in many textbooks.⁴ That is, if the rate constant of a bimolecular reaction is

$$k = ZPe^{-E/RT} \quad (2)$$

where Z is the rate constant for collision of the reacting pair, P is a probability that a collision will be reactive when the exponential terms approaches unity, and E is an energy barrier, then the equilibrium constant, K_{eq}, must be equal to

$$K_{\text{eq}} = \frac{k_f}{k_r} = \frac{Z_f P_f e^{-E_f/RT}}{Z_r P_r e^{-E_r/RT}} = \frac{Z_f P_f}{Z_r P_r} e^{-(E_f - E_r)/RT} = e^{\Delta S/R_c - \Delta H/RT} \quad (3)$$

(where the subscript f refers to the forward or exothermic direction of reaction, and the subscript r refers to the reverse or endothermic direction). Then, since $e^{-(E_f - E_r)/RT}$ can be equated to $e^{-\Delta H/RT}$ (for ion-molecule reactions, E_f is usually

zero and E_r is just $-\Delta H$), it follows that

$$\Delta S = R \left[\ln \frac{Z_f}{Z_r} + \ln \frac{P_f}{P_r} \right] \quad (4)$$

In the case of ion-molecule reactions, there are numerous examples in the literature⁵ of reactions for which P is close to unity. That is, for many exothermic ion-molecule reactions $k_f = Z_f$, within experimental error. For ion-molecule collisions, the collision rate constants, Z, can be readily calculated.⁶ Table I shows that, even under conditions such that the reaction in the reverse direction can occur, P may be unity. Table II shows that P may be unity in the endothermic direction also, so that in many ion-molecule equilibria the enthalpy of reaction may be predicted simply from the rate constant of the reverse reaction.

This implies that eq 4 is valid for ion-molecule reactions. The results given in Tables I and II demonstrate that it is not the case that the mechanism of the equilibrium might include some compensating occurrence such that the ratio Z_f/Z_r in eq 3 and 4 would be effectively cancelled by components of the ratio P_f/P_r.

Thus it can be concluded from these results that, in any ion-molecule equilibrium in which the entropy is not experimentally determined, the estimation of the intermolecular

entropy term can be based on the term $R \ln (Z_f/Z_r)$. Most calculations of entropy changes in ion-molecule equilibria have been based on ratios of partition functions expressing the distributions of internal energy in the separated reactant and product species. These partition functions are derived from a model of the system which assumes that interactions, such as those taken into account in calculating Z_f and Z_r , do not exist. The inclusion of a term $R \ln (Z_f/Z_r)$ in the entropy merely reflects the fact that, in the particular case of equilibria involving ions, such interactions do play a role. According to thermodynamics, the calculation of ΔS from statistical mechanics involves two parts, that arising from the ratios of internal partition functions (the "ideal" contribution) and that arising from the effects of the intermolecular forces on the configuration integral. The latter contribution is generally expressed in terms of the fugacity, which is usually derived from the experimentally observed pressure-volume-temperature relationships of a gas or from van der Waals constants. Obviously the fugacities of ions are not experimentally accessible in these ways. However, a calculation⁷ of the contribution to ΔG° by intermolecular interactions is based on a consideration of the same potential functions which are the basis for the calculation of Z . Hence, it is to be expected that a statistical mechanical derivation of ΔS for ion-molecule equilibria would result in expressions which are equivalent to those derived here from kinetic considerations.

Table III lists some values of ΔS which are derived from the results of Meot-Ner and Field,^{3d} who determined ΔG° for charge-transfer equilibria in aromatic systems at 450 and 600 K. Since the changes in ΔG° over this temperature range are small (± 0.3 kcal/mol), these authors concluded that the entropy change for charge-transfer equilibria in these systems is zero. The comparisons shown in Table III demonstrate that, for all the reaction pairs studied by those authors in which there should be no other contributions to the entropy, the sign of the entropy change is always correctly predicted from the collision contribution. (In these measurements the experimental error is of approximately the same magnitude as the entropy change being determined.) Table III also shows the only entropy determinations in the literature^{2a} for proton-transfer equilibria in which it is predicted there should be no other contributions to the entropy change. The collision contribution correctly predicts the sign and approximately the magnitude of the measured entropy change.

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- (6) The collision rate constants, Z , are usually calculated using the Langevin-Gioumouis-Stevenson formalism (P. Langevin, *Ann. Chim. Phys.*, **5**, 245 (1905); G. Gioumouis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958)) for reactions involving nonpolar molecules, $Z = 2\pi e(\alpha/\mu)^{1/2}$, or the Su-Bowers A. D. O. formalism (T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 347 (1973); T. Su and M. T. Bowers, *J. Am. Chem. Soc.*, **95**, 1370 (1973); M. T. Bowers and T. Su in ref 2d, p 163) for reactions involving molecules having a permanent dipole moment, $Z = 2\pi e/\mu^{1/2}[\alpha^{1/2} + c\mu_D/(2/\pi kT)^{1/2}]$, (where α is the polarizability of the molecule, e is the charge on the electron, μ is the reduced mass of the colliding pair, μ_D is the permanent dipole, and c is a parameter having values between 0 and 1 which is a function of $\mu_D/\alpha^{1/2}$) or the alternative approach recently proposed by Barker and Ridge (R. A. Barker and D. P. Ridge, *J. Chem. Phys.*, **64**, 4411 (1976)). All of these models are based on a calculation of the attractive potential existing between the ion and molecule because of interactions between the charge and the induced dipole or permanent dipole of the molecule. Although these calculations do not take into account certain terms in the ion-molecule potential of interaction (such as quadrupole moments, for instance), more complete calculations, as well as comparisons with experimentally determined ion-molecule collision rates, indicate that these equations predict the value of Z correctly, within 15-20%.
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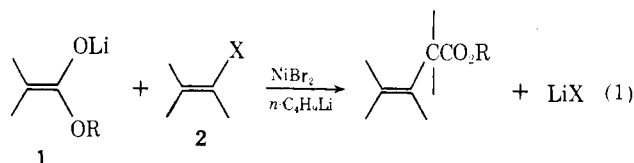
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A Nickel Catalyst for the Arylation and Vinylation of Lithium Ester Enolates

Sir:

α -Aryl and α -vinyl carbonyl groupings are structural features of a large number of biologically important molecules. A method for the direct arylation or vinylation of enolate anions would greatly simplify the synthesis of such molecules. Progress to this goal has been reported by a number of workers,¹ with perhaps the most promising approach to date being the trapping of photogenerated aryl radicals with ketone enolates (the $S_{RN}1$ reaction).²

We wish to report that the addition of *n*-butyllithium to suspensions of nickel(II) bromide in tetrahydrofuran (THF) at dry ice temperature forms material which catalyzes an efficient substitution reaction of lithium ester enolates (**1**) with aryl or vinyl halides (**2**) (eq 1). The reaction occurs with clean



retention of stereochemistry at the halogen-bearing carbon, as judged from results obtained with the configurational isomers of β -bromostyrene (eq 2, 3).³

The reaction with the lithium enolate of ethyl crotonate (**5**) occurs at the γ carbon to give chain extended vinylation or

