

Table I

Solvent	% enol acetate, $\pm 2$	% Va (cis) <sup>a,b</sup>	% Vb (trans) <sup>a,b</sup>	Solvent shell-equatorial methyl interaction, kcal./mole <sup>c</sup>
Tetrahydrofuran	67.3	63.7	36.3	0.57
N,N-Dimethylacetamide	66.8	61.7	38.3	0.61
Benzene	46.8	61.6	38.4	0.61
Ether	53.2	59.1	40.9	0.68
Monoglyme	59.9	56.2	43.8	0.76
Diglyme	68.0	55.0	45.0	0.78
Dioxane	55.2	52.4	47.6	0.84
Hexamethylphosphoramide	73.4	50.8	49.2	0.88
Dimethylformamide	65.7	47.8	52.2	0.95
Dimethyl sulfoxide	66.8	44.9	55.1	1.02
Sulfolane	52.4	44.8	55.2	1.02
Triglyme	47.2	38.6	61.4	1.18

<sup>a</sup> In these solvents the equilibrium percentage of *cis* (Va) isomer is in the range of 90–92% (cf. ref. 7) as determined by g.l.p.c.

<sup>b</sup> Corrected percentages based on the isomeric distribution of free ketone under equilibrating conditions. <sup>c</sup> Based on the assumption that a diaxial 1,3-methyl-hydrogen interaction in cyclohexane has an energy value of 0.9 kcal./mole.

lead to substantially greater alkylation than might be anticipated of the more substituted enolate anion III (which is in equilibrium with II). As one of the controlling influences in enolate anion alkylation, this factor appears not to have been recognized thus far.

Studies along these lines are continuing.<sup>10</sup>

**Acknowledgment.** We wish to thank Mr. D. F. Moakley for technical assistance and Mr. John Flynn for the determination of mass spectra of the deuterated ketones.

(10) Ringold and co-workers (private communication) have found in the case of the potassium enolate derived from 2-methylandro-4-ene-3,17-dione in *t*-butyl alcohol solution that the steric interaction of the equatorial methyl group and the solvated ion pair (as in IIa) destabilizes the enolate by almost 2 kcal./mole.

Sudarshan K. Malhotra, Francis Johnson

The Dow Chemical Company, Eastern Research Laboratory  
Wayland, Massachusetts

Received August 30, 1965

### The Role of Vibrational Excitation in Hydrogen-Deuterium Exchange. Nascent Molecules at Room Temperature

Sir:

Kinetic studies of a variety of homogeneous gas-phase H-D exchange reactions at elevated temperatures in shock tubes have led to an unexpected and novel conclusion: that the exchange rate is limited by the rate of populating critical vibrational levels.<sup>1-3</sup> The implication of this mechanism, which accounts for the shock-tube data in detail, is that for the strictly bimolecular process the relative kinetic energy of transla-

(1) A. Lifshitz, C. Lifshitz, and S. H. Bauer, *J. Am. Chem. Soc.*, **87**, 143 (1965).

(2) S. H. Bauer and E. L. Resler, Jr., *Science*, **146**, 1045 (1964).

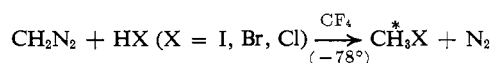
(3) S. H. Bauer and E. Ossa, presented before the Division of Physical Chemistry, at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, Abstract No. 115.

tional motion along the line of centers of the colliding pair is of little consequence. The transition probability for exchange is high only when the four-center transition state is generated by the association of a pair of molecules, one of which is in a high enough vibrational level. The vibrational excitation mechanism (a) accounts for the observed diverse power rate expressions, such as that for H<sub>2</sub> + D<sub>2</sub>

$$\frac{d(\text{HD})}{dt} = k_p(\text{D}_2)^{0.66}(\text{H}_2)^{0.38}(\text{Ar})^{0.93}$$

(b) accounts for the narrow range of activation energies for exchange (for example, with ammonia it is approximately 39 kcal./mole, with hydrogen 42 kcal./mole, with methane 52 kcal./mole; (c) permitted the *a priori* calculation of the pre-exponential factor for the exchange rate between hydrogen and deuterium from the observed vibrational relaxation times,<sup>4</sup> to within a factor of five. Further, an extension of this mechanism to the reactions C<sub>2</sub>N<sub>2</sub> + H<sub>2</sub> → 2HCN and C<sub>2</sub>N<sub>2</sub> + D<sub>2</sub> → 2DCN predicted that the rate of the latter is severalfold faster than that of the former. We found that DCN/HCN = 6 (1050°K.), 3 (1130°K.), 1.6 (1200°K.).

While the indirect evidence is impressive, it is difficult to demonstrate directly that the exchange rate is insensitive to the relative translational energy of the colliding pair. In contrast, the demonstration of the second half of the postulate, that vibrational excitation in the absence of any significant translational contribution is sufficient for exchange, has now been made. In this proof we utilized the very interesting reaction reported recently by Hassler and Setser<sup>5</sup> on the homogeneous gas phase reaction of diazomethane with mineral acids. They found that



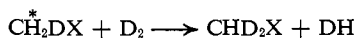
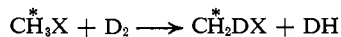
Their explorations showed that whereas CH<sub>3</sub>I is sufficiently activated (approximately 60 kcal./mole) to decompose unimolecularly to CH<sub>3</sub> + I, in CH<sub>3</sub>Br and CH<sub>3</sub>Cl the bond-dissociation energies for the corresponding C-X bonds are greater than the available excitation energy and avoid decomposition. *No radicals could be detected in these mixtures.* These facts we accept without further tests; however, our analytical data indirectly support their conclusions.

We found that when the reaction between diazomethane and HBr (or HCl) was carried out at room temperature using D<sub>2</sub> or CD<sub>4</sub> as diluents, a significant fraction of the alkyl halides appeared as CH<sub>2</sub>DX. This is due to H-D atom exchange which occurs at room temperature between the nascent, vibrationally activated CH<sub>3</sub>X and either D<sub>2</sub> or CD<sub>4</sub>. Were the energy released during the reaction to appear as relative translational energy of the two product molecules, only 23% (≈14 kcal./mole) could be carried by the methyl bromide, and this is insufficient for exchange activation. Further evidence for this conclusion was provided by the reaction between diazomethane and DX

(4) J. H. Kiefer and R. W. Lutz, *Phys. Fluids*, **8**, 1393 (1965), and private communication.

(5) J. C. Hassler and D. W. Setser, *J. Am. Chem. Soc.*, **87**, 3793 (1965).

with argon as the diluent; a significant amount of  $\text{CHD}_2\text{X}$  was produced. Indeed, to account fully for all the observations we are forced to the conclusion that, after the first atom switch, sufficient vibrational excitation is retained in the singly exchanged product so that a second atom switch occasionally occurs prior to de-excitation by collision.



Typical data are given in Table I. At the present time we are in the process of designing and executing quantitative experiments to measure: (1) the relative efficiencies for de-excitation and for exchange by various diluent gases; (2) the temperature dependence of the ratio of de-excitation to exchange rates, in order to obtain some measure of the role of translational energy; (3) the local temperature distributions in the mixing zone; (4) the absolute rates of the reaction by using rapid flow systems; (5) kinetic isotope effects in reactions between  $\text{CH}_2^*\text{DX}$  and  $\text{HD}$ , and  $\text{CD}_2^*\text{HX}$  and  $\text{HD}$ ; and (6) to look for infrared emission from the reaction zone as the total pressure and fraction of diluent are reduced.

Table I. Typical Product Distribution

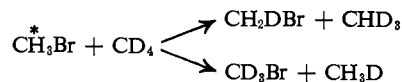
Reactants (temp., °C.) <sup>a</sup>	Diluent	Product analysis <sup>b</sup>
$\text{CH}_2\text{N}_2$ , HBr (25.1)	$\text{CD}_4$	$\text{CH}_3\text{Br}$ (80), $\text{CH}_2\text{DBr}$ (12), $\text{CHD}_2\text{Br}$ (8)
$\text{CH}_2\text{N}_2$ , HBr (44.5)	$\text{D}_2$	$\text{CH}_3\text{Br}$ (78), $\text{CH}_2\text{DBr}$ (19), $\text{CHD}_2\text{Br}$ (3)
$\text{CH}_2\text{N}_2$ , DBr [HBr] (45.3)	$\text{CH}_4$	$\text{CH}_3\text{Br}$ (47), $\text{CH}_2\text{DBr}$ (40), $\text{CHD}_2\text{Br}$ (13)
$\text{CH}_2\text{N}_2$ , DBr [HBr] (19.6)	He	$\text{CH}_3\text{Br}$ (41), $\text{CH}_2\text{DBr}$ (44), $\text{CHD}_2\text{Br}$ (11), $\text{CD}_3\text{Br}$ (4)
$\text{CH}_2\text{N}_2$ , DBr [HBr] (-27.5)	$\text{CH}_4$	$\text{CH}_3\text{Br}$ (52), $\text{CH}_2\text{DBr}$ (43), $\text{CHD}_2\text{Br}$ (5)
$\text{CH}_2\text{N}_2$ , DCl [HCl] (25.0)	Ar	$\text{CH}_2\text{Cl}$ (15), $\text{CH}_2\text{DCl}$ (59.4), $\text{CHD}_2\text{Cl}$ (18), $\text{CD}_3\text{Cl}$ (7.3)

<sup>a</sup> The brackets indicate impurity present. <sup>b</sup> Per cent yield in parentheses.

Diazold (N-methyl-N-nitroso-*p*-toluenesulfonamide) was used as the precursor of  $\text{CH}_2\text{N}_2$ , which was generated *in vacuo* by the technique of Dessaux and Durand.<sup>6</sup> It was dried by passing through potassium hydroxide pellets and stored at the required pressure in a 5-cc. bulb. An equal pressure of diluent gas was added at a total pressure of  $\approx 100$  mm. The reaction vessel was a 250-cc. bulb with a 1-mm. bore capillary inlet tube leading to its center. The reactor and capillary were surrounded by a dewar to maintain the system at the desired temperature. The bulb was filled to a total pressure of 20 mm. with a 1:10 mixture of hydrogen bromide (or DBr or HCl) and the diluent gas (Ar,  $\text{CD}_4$ ,  $\text{D}_2$ ). Using a constricted inlet, on opening the stopcock, gas flowed into the reaction vessel over a period of about 1 sec. The gases were allowed to mix for 24 hr. before removing a sample for analysis by mass spectrometry. The mass spectral patterns for methyl bromide, methane, and the deuteriomethanes were obtained using authentic samples (and correcting

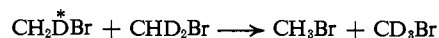
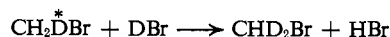
(6) O. Dessaux and M. Durand, *Bull. soc. chim. France*, 41 (1963).

for impurities). The cracking patterns for the deuterio-methyl bromides were not available; these were computed from the pattern for methyl bromide and the  $\text{C}^{12}/\text{C}^{13}$  isotope ratio. The reaction



was studied at 25.1°. Product distribution showed that no more than 1% exchange of the bromine atom occurred to give methyl- $d_3$  bromide but there was about 12% H-D exchange to produce methyl- $d_1$  bromide.

Diazomethane reacts with deuterium bromide to give methyl- $d_1$  bromide. However, if the lifetime of the activated molecule is long, further reaction may occur. Using a 1:10 mixture of deuterium bromide in argon at room temperature, mass spectral analysis showed that the products included methyl- $d_3$  and methyl- $d_2$  bromide as well as methyl- $d_1$  bromide. These can only be accounted for by the assumption that there is subsequent reaction of the activated methyl- $d_1$  bromide with deuterium bromide.



The experiment was repeated using a 24.5:1 mixture of helium and deuterium bromide at room temperature. Since helium is a more efficient deactivator than argon, the percentages of methyl- $d_3$  and methyl- $d_2$  bromides were reduced by factors of five and two, respectively, as expected.

*Acknowledgments.* This work was supported by the N.A.S.A. under Grant Nsg 116-61 and by the A.E.C. under Contract AT(30-1)-3211, to whom grateful acknowledgment is made.

S. H. Bauer, David Marshall, Tomas Baer  
Department of Chemistry, Cornell University  
Ithaca, New York  
Received October 7, 1965

### Preparation of the Ketone Tautomer of a Phenol by a Cope Rearrangement<sup>1</sup>

Sir:

It has recently been suggested that steric repulsions between *o-t*-butyl groups should tend to convert 3,4-di-*t*-butylphenol to its nonplanar ketonic tautomer.<sup>2</sup> Although the reactions of the phenol and of 3,4-di-*t*-butylaniline suggested that the tautomeric forms were readily formed, no direct evidence for the presence of the tautomers could be obtained.<sup>2</sup> We now wish to report that the presence of a *t*-butyl group at C-3 can allow preparation of the ketonic form of a phenol by thermal processes.

Irradiation of 4-allyl-2,6-di-*t*-butyl-4-methylcyclohexa-2,5-dienone (**1**)<sup>3</sup> in the manner previously described<sup>4</sup> gave a product whose infrared spectrum ( $\lambda_{\text{max}}$  6.05 and 6.35  $\mu$ ) and ultraviolet spectrum in methanol [ $\lambda_{\text{max}}$  309  $m\mu$  ( $\epsilon$  3045)] suggested that it consisted mainly of the

(1) Reactions of Cyclohexadienones. XIV. Part XIII: B. Miller, *J. Am. Chem. Soc.*, 87, 5115 (1965).

(2) A. W. Burgstahler, P. L. Chien, and M. O. Abdel-Rahman, *ibid.*, 86, 5281 (1964).

(3) B. Miller, *J. Org. Chem.*, 30, 1964 (1965).

(4) B. Miller and H. Margulies, *Chem. Commun.*, 314 (1965).