

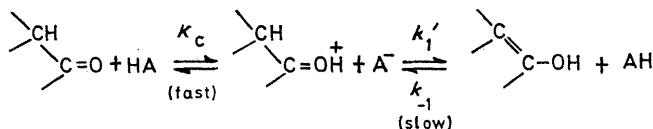
Kinetic Analysis of the Bromination of Acetone in an Acidic Medium: Solvent Isotope Effect on the Rate of Enol Ketonization

By J. E. DUBOIS* and J. TOULLEC

(Laboratoire de Chimie Organique Physique de la Faculté des Sciences de Paris, Associé au CNRS, 1, rue Guy de la Brosse, Paris 5^e, France)

Summary The solvent isotope effect on the ketonization of acetone enol demonstrates the similarity of this reaction and the hydrolysis of enol ethers.

INVESTIGATION of the transition state for ketone enolization is made difficult by the existence of a rapid pre-equilibrium preceding the slow step. The reverse reaction, ketonization (which involves the same transition state), does not suffer the same inconvenience.



Kinetic analysis of the bromination of acetone allows us to determine the relative rates of the bromination and ketonization of the enol. If the reasonable assumption that the bromination rate is identical¹ in H₂O and D₂O is made, the solvent isotope effect on the ketonization rate, otherwise inaccessible, can be determined.

We have used this approach to study the bromination of acetone in the presence of sulphuric acid.

At high acidity, for very low concentrations of bromine, two apparent rate constants can be determined:² the catalytic enolization constant, $k_1 = K_c \times k_1'$, and the apparent enol bromination constant, $k_{\text{II}} = k_1 \times k_{\text{Br}_2}/k_{-1}$.

Solvent isotope effects on the kinetic constants of the bromination of acetone, at 25°,^a in water.

(H₂SO₄-D₂SO₄ = 0.25 M; NaBr = 0.2 M)

Atomic isotopic fraction (<i>n</i>)	10 ⁵ <i>k</i> ₁ (l.mole ⁻¹ sec. ⁻¹)	<i>k</i> _{II} (l.mole ⁻¹ sec. ⁻¹)	10 ⁶ <i>r</i> = 10 ⁶ × <i>k</i> ₁ / <i>k</i> _{II}
0	2.62	9.67	2.71
0.199	2.85	11.5	2.48
0.399	3.12	13.7	2.28
0.599	3.47	17.6	1.97
0.798	3.70	25.5	1.45
0.998	4.23	53.3	0.793

^a Rate constants were determined by coulombometry (J. E. Dubois, P. Alcais, and G. Barbier, *J. Electroanal. Chem.*, 1964, **8**, 359) for acetone concentration of 2 × 10⁻² M, and for initial bromine concentrations of ca. 10⁻⁷–10⁻⁵ M. Standard deviations ca. 2%.

where k_{Br_2} is the second-order rate constant for the bromination of the enol by the $\text{Br}_2/\text{Br}_3^-$ system. Then $k_1/k_{\text{II}} = k_{-1}/k_{\text{Br}_2} = r$, the ratio of the rate constants for the electrophilic additions of bromine and proton.

The inverse isotope effect on the enolization rate (0.62) is in accordance with that recently⁸ reported and corresponds to a two-step mechanism.

The isotope effect on r (3.4) is close to the theoretical maximum (3.6) expected for reactions of this type, when the degree of proton transfer in the transition state is close to 0.5.⁴

The Figure compares values of r for $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures with the curves calculated for various values of the Brønsted exponent α , from the Gold-Kresge equation.⁵ The value of α , which is considered to be a measure of the degree of proton transfer in the transition state,⁶ is therefore close to 0.5. This result is in good agreement with that predicted ($\alpha = 0.55$) by the kinetic analysis of enolization catalysed by different weak acids.⁷

In the hydrolysis of enol ethers, in particular the hydrolysis of ethyl isopropenyl ether, the ether analogue of acetone enol, virtually the same isotope effect (3.5) is observed. Given the estimated value^{2a} of between 18 and 33 $\text{l.mole}^{-1} \text{sec.}^{-1}$ for k_{-1} (H_2O), the point corresponding to an isotope effect of 3.4 fits the Kresge-Sagatys-Chen correlation⁸ for hydrolysis of enol ethers remarkably well. There is a clear analogy between the mechanisms of the hydrolysis of enol ethers and the ketonization of enols. The rate-determining step is the same in both cases and the transition states have very similar structures.

The assumption that $k_{\text{Br}_2}(\text{H}_2\text{O})/k_{\text{Br}_2}(\text{D}_2\text{O}) = 1$ will be tested by further studies. However the coherence of these results suggests that this hypothesis is approximately correct.

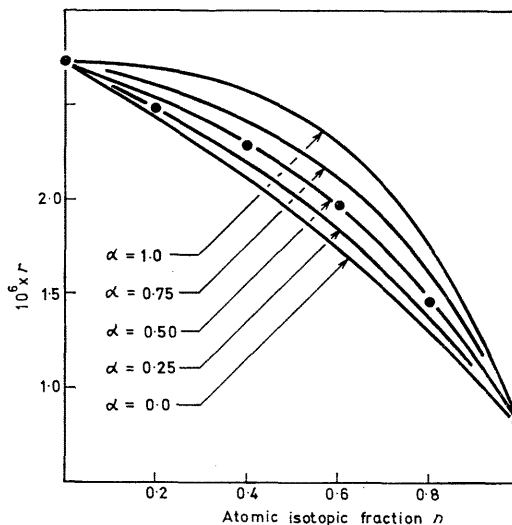


FIGURE. Effect of solvent isotope composition on relative rates of ketonization and enol bromination.

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¹ Studies of solvent effects in the bromination of olefins (J. E. Dubois and F. Garnier, *Bull. Soc. chim. France*, 1968, 3797) suggest that if any isotope effect on the bromination of enols exists it will be direct rather than inverse. The ratio $r(\text{H}_2\text{O})/r(\text{D}_2\text{O})$ must, therefore, represent a minimum value for the isotope effect on the ketonization rate.

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