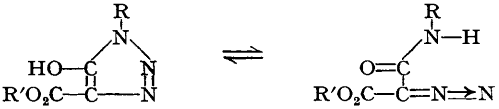
# 257. *The Mechanism of the Tautomeric Change of 5-Hydroxy-1 : 2 : 3-triazole-4-carboxylic Esters into Aliphatic Diazo-compounds.*

By B. R. Brown and D. Ll. Hammick.

Dimroth (*Annalen*, 1904, **335**, 1; 1905, **338**, 143; 1910, **373**, 336) interpreted the kinetics of this reaction as showing that the change takes place in the un-ionised enol molecule. A reconsideration of his data indicates that the change is bimolecular, involving a proton and an enol ion. The electronic processes involved in the proposed mechanism are deduced from a comparison of rate constants for various substituted triazole esters.

The reaction under consideration is the following:



(I; R′ = Me or Et.)

which was established by Dimroth (*loc. cit.*). Owing to the fact that the enolic triazole tautomer is acidic, he was able to study the kinetics of the forward reaction and the equilibrium in various solvents. He interpreted his results as showing that the reaction is unimolecular with respect to the enol, and concluded that the change from enol to neutral form takes place in the un-ionised enol molecule. His evidence (*Annalen*, 1904, **335**, 60) was the observed proportionality between the rate in the presence of various concentrations of the sodium salt of the enol, and the amount of undissociated enol as calculated from the " degree of dissociation " of the sodium salt obtained from conductivity data. His conclusion is invalid on account both of this fallacious " degree of dissociation ", and of the occurrence of an appreciable salt effect.

A reconsideration of Dimroth's results in the light of more recent ionic and kinetic theory shows that the reaction is in reality a bimolecular process involving a hydrogen ion and an enol ion. Thus his values (*ibid.*, p. 53) for the rate constants in the presence of water and of 0·06N-sodium chloride :

$k$ (mins.$^{-1}$) at 50° in water (I; R = phenyl) = 0·00128
$k$ (mins.$^{-1}$) at 50° in 0·06N-NaCl (I; R = phenyl) = 0·00106

reveal a negative salt effect and indicate that the reaction is between two oppositely charged ions. Also his unimolecular rate constants increase as the concentration of either the hydrogen ion or the enol ion increases (*ibid.*, p. 54) :

$k$ (mins.$^{-1}$) at 50° in water (I; R = phenyl) = 0·00128
$k$ (mins.$^{-1}$) at 50° in dilute HCl (I; R = phenyl) = 0·00195

| Mols. of Na salt of enol : mols. of enol. | $k$ (mins.$^{-1}$). |
|---|---|
| 0 : 1 | 0·00128 |
| 1 : 1 | 0·00195 |
| 2 : 1 | 0·00225 |
| 4 : 1 | 0·00267 |
| 8 : 1 | 0·00306 |

Addition of alkali causes an increased rate of reaction by increasing the concentration of enol ion. This fact is remarked upon by Dimroth (*ibid.*, p. 3), and prevents an ordinary alkali titration being used to follow the reaction.

Following up this evidence, Dimroth's results (*ibid.*, p. 49) for the tautomerism of (I; R = phenyl) in water have been recalculated using a bimolecular rate equation. His values (*ibid.*, 1905, **338**, 175; 1904, **335**, 57) for the dissociation constant of this compound in water are :

$$K \text{ at } 25° = 1{\cdot}6 \times 10^{-2}$$
$$K \text{ at } 50° = 1{\cdot}3 \times 10^{-2}$$

whence the value at 40° is estimated at $1{\cdot}4 \times 10^{-2}$. Using these dissociation constants and the following equations for the estimation of the enol,

$$6(C_{10}H_8O_2N_3)OH + 5KI + KIO_3 = 6(C_{10}H_8O_2N_3)OK + 3H_2O + 3I_2$$
$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI,$$

the following typical sets of results were calculated :

25 *C.c. of reaction mixture titrated against* N/50-*thiosulphate* (*temp.*, 50°).

| Time (mins.). | Titre (c.c.). | [H+] = [enol ion]. (mols./l.). | Bimol. $k$ (mols./l./sec.). | Dimroth's unimol. constant 0·4343$k$ (mins.$^{-1}$). |
|---|---|---|---|---|
| 0 | 18·55 | $0{\cdot}884 \times 10^{-2}$ | | |
| 60 | 17·10 | 0·834 ,, | $1{\cdot}88 \times 10^{-3}$ | $5{\cdot}89 \times 10^{-4}$ |
| 120 | 15·85 | 0·789 ,, | 1·94 ,, | 5·69 ,, |
| 180 | 14·68 | 0·747 ,, | 1·92 ,, | 5·65 ,, |
| 300 | 12·62 | 0·667 ,, | 2·05 ,, | 5·57 ,, |
| 400 | 11·13 | 0·607 ,, | 2·15 ,, | 5·54 ,, |
| | | Average : | 1·99 ,, | |
| | | Average for a similar set at 50° : | 1·88 ,, | |

100 *C.c. of reaction mixture titrated against* N/10-*thiosulphate* (*temp.*, 40·2°).

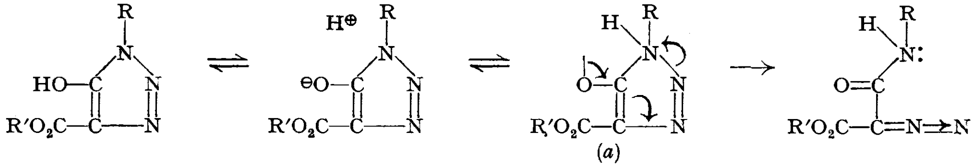
| | | | | |
|---|---|---|---|---|
| 0 | 12·77 | $0{\cdot}809 \times 10^{-2}$ | | |
| 170 | 12·13 | 0·779 ,, | $4{\cdot}67 \times 10^{-4}$ | $1{\cdot}31 \times 10^{-4}$ |
| 300 | 11·70 | 0·759 ,, | 4·53 ,, | 1·27 ,, |
| 380 | 11·47 | 0·748 ,, | 4·46 ,, | 1·23 ,, |
| 470 | 11·15 | 0·732 ,, | 4·61 ,, | 1·21 ,, |
| | | Average : | 4·57 ,, | |

Whence, $k_{50^\circ} = 1·94 \times 10^{-3}$ and $k_{40·2^\circ} = 4·57 \times 10^{-4}$, both in mols./l./sec. Substitution in the equation $k = PZe^{-E/RT}$ gives the following $E$ and $PZ$ values :

$$E = 29,660 \text{ cals.} \qquad PZ = 10^{+17·3}$$

It is seen that the $PZ$ value is one normally observed for a reaction between oppositely charged ions, *viz.*, $10^{+13}$ to $10^{+19}$ (Bell, *J.*, 1943, 629), and therefore supports a bimolecular ionic mechanism.

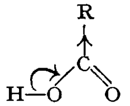
These considerations lead us to suggest the following picture of the tautomeric change :



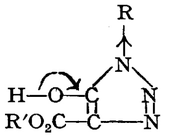
Evidence that the electronic processes implied in (*a*) for the decomposition of the transition state are rate-determining is obtained by a consideration of the effects of substituents on the rate constants and on the equilibrium constants. These will be expected to parallel the dissociation constants of the enol, which in turn should parallel the dissociation constants of the corresponding acids, R·CO$_2$H. That the latter is the case is evident from Dimroth's determination of the dissociation constants of various enol forms :

| R. | R·CO$_2$H. (Watson, " Modern Theories of Organic Chemistry," 2nd Edition, 1941, p. 27.) | Enol. (Dimroth, *Annalen*, 1905, **338**, 175.) |
|---|---|---|
| Methyl | $1·82 \times 10^{-5}$ | $0·3 \times 10^{-2}$ |
| *p*-Tolyl | 4·24 ,, | 1·0 ,, |
| Phenyl | 6·27 ,, | 1·6 ,, |
| *p*-Bromophenyl | 10·7 ,, | 2·0 ,, |

It is seen that the dissociation constants increase with the power of the group R to accept electrons, as expected for the comparable processes :



and



The electronic processes (*a*) in the proposed mechanism should likewise be facilitated by acceptor groups at R, and hence the rate and equilibrium constants (diazo-compound/triazole) should increase in the same order as the ionisation constants, *i.e.*, with the accepting power of R. That this does occur is good evidence for the proposed electron shifts.

*Values of* K *and* k *in ethyl alcohol at* 25°.

(Dimroth, *Annalen*, 1910, **373**, 349.)

| R. | *K*. | *k* (mins.$^{-1}$). |
|---|---|---|
| Benzyl | 118 | $0·003 \times 10^{-2}$ |
| *p*-Tolyl | 120 | 0·94 ,, |
| Phenyl | 300 | 1·02 ,, |
| *p*-Bromophenyl | 555 | 4·58 ,, |
| *p*-Nitrophenyl | very large | 60·0 ,, |
| 2 : 4-Dinitrophenyl | not measurable | 100·0 ,, |

Thus Dimroth's kinetic data indicate that the reaction has an ionic mechanism, involving the attack of a proton on an enol ion, and furthermore, enable the nature of the electronic shifts involved to be elucidated with a fair degree of certainty.

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