A Calculation of the Equilibria in KetoEnol Tautomerism

G. W. Wheland

The Nature of the Chemical Bond. V

LINUS PAULING AND G. W. WHELAND, *California Institute of Technology, Pasadena*

In this paper a number of numerical errors appeared. The corrected values are given below.

Substitute the following for the corresponding lines in Table III, p. 370:

Radical	W'	W	$W-W'$
Biphenylmethyl	$Q+ 3.8000\alpha$	$Q+ 4.4473\alpha$	0.6473α
Phenylfluoryl	$Q+ 5.2000\alpha$	$Q+ 6.2764\alpha$	1.0764α
Biphenyldiphenylmethyl	$Q+ 7.6000\alpha$	$Q+ 8.7738\alpha$	1.1738α
Phenyldibiphenylmethyl	$Q+ 9.5000\alpha$	$Q+10.7347\alpha$	1.2347α
Tribiphenylmethyl	$Q+11.4000\alpha$	$Q+12.6905\alpha$	1.2905α

And in Table IV, p. 371:

Radical	Position of odd electron	Number of structures	Relative values of coefficients
Biphenylmethyl	methyl carbon	4	1
	biphenyl group	9	0.5608
Biphenyldiphenylmethyl	methyl carbon	16	1
	phenyl group	48	0.8861
	biphenyl group	36	0.7816
Phenyldibiphenylmethyl	methyl carbon	32	1
	phenyl group	48	0.8433
	biphenyl group	144	0.7392
Tribiphenylmethyl	methyl carbon	64	1
	biphenyl group	432	0.7007

The discussion in section (c), page 373, regarding the quantitative agreement of the calculations with experiment has to be altered somewhat in accordance with the corrected values of the free radical resonance energies. The calculated dissociation constant of hexabiphenylethane now becomes $(3.0)^{18}\times4.1\times10^{-4}=1.6\times10^5$. This value is in good agreement with the reported complete dissociation of the molecule, but may be too high. In general, the constants found in this manner for the various hexaarylethanes seem to be uniformly too large, in comparison with that of hexaphenylethane. This discrepancy may perhaps arise from the neglect of excited structures or may be due to the fact that we are comparing small differences between larger quantities. A third possibility is that the value of α assumed in the calculations is too large (in absolute magnitude). This would be in accordance with the views of Penney.[22] It is significant, however, that the qualitative agreement with experiment is now perfect, the empirical order given on page 368 being reproduced without error.

[22] W. G. Penney, Proc. Roy. Soc. A144, 166 (1934).

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Delete the diagonal bonds extending from R to the carbonyl carbon atom in structures XII–XVI inclusive (page 733).