

## Detritiation of Various Fluorenes in Highly Basic Media

By Derek W. Earls, John R. Jones,\* and Trevor G. Rumney, Chemistry Department, University of Surrey, Guildford GU2 5XH

Anthony F. Cockerill, Lilly Research Centre, Erl Wood Manor, Windlesham, Surrey

Rates of detritiation from the 9-position of fluorene, 9-phenyl-, and 9-*t*-butyl-fluorene have been measured at 25° in hydroxide-water solutions containing various amounts of dimethyl sulphoxide. In all three cases considerable rate enhancements are observed with the tendency being, as reflected in the  $\log k$  vs.  $H_-$  correlations, for the weaker acid to be the more receptive to increases in basicity. These results are in accord with previous findings for other carbon acids.

DIPOLAR aprotic solvents and in particular dimethyl sulphoxide (DMSO) have the ability to increase considerably the basicity of an aqueous hydroxide ion solution. Thus the acidity function  $H_-$  ( $-\log a_{\text{H}^+}/f_{\text{HA}}$ ) of a 0.01M aqueous solution of tetramethyl ammonium hydroxide increases from 12 to 26 in going from a zero to a 99.5 mole % dimethyl sulphoxide medium.<sup>1</sup> Complementary studies on the hydroxide-catalysed ionisation of various carbon acids have demonstrated equally dramatic increases in rates.<sup>2</sup> The possibility therefore exists that many reactions which proceed too slowly in aqueous conditions to be of commercial value in an industrial process can, when carried out in highly basic media, become more viable. Only very recently it has been shown that the simple but nevertheless very important reaction<sup>3</sup> between molecular hydrogen (or deuterium) and hydroxide ions in aqueous solution, leading to *ortho*-*para*-conversion (or isotopic exchange) was accelerated by a factor of  $10^4$  as the medium composition changed from 0 to 99.5 mole % dimethyl sulphoxide.

It is not possible at present to predict with any certainty the magnitude of these rate enhancements. A better understanding of the factors involved may be obtained by studying compounds which have also served as indicators in setting up the  $H_-$  scale; alternatively they may closely resemble the indicators in their structure. The carbon acids so far employed have been activated by carbonyl,<sup>4-6</sup> sulphonyl,<sup>7</sup> cyano,<sup>8-11</sup> nitro,<sup>12</sup> and chloro-groups.<sup>11</sup> In addition Bowden and Cook<sup>13</sup> have investigated the base-catalysed isomerisation of a series of 3- and 4-substituted allylbenzenes but these compounds are still somewhat removed from the fluorenes employed to set up a carbon acid based  $H_-$  scale.<sup>14</sup> Although the detritiation of fluorene has been studied in concentrated methanolic sodium methoxide solutions<sup>15,16</sup> the importance of ion-association effects in this system makes a satisfactory interpretation of rate-equilibria correlations very difficult. This point is reinforced by the recent finding<sup>17</sup> of a proton-transfer reaction in ethanolic

ethoxide solutions where some of the ion pairs were found to be more reactive than the free ions. Consequently we have in the present study employed DMSO-OH<sup>-</sup>-H<sub>2</sub>O as our basic system (ion-association effects are unimportant at low base concentrations) and three fluorenes, 9-*t*-butyl, 9-phenyl, and fluorene itself, as the substrates.

### EXPERIMENTAL

**Materials.**—DMSO was dried over 4A molecular sieves before being fractionally distilled under reduced pressure in the presence of nitrogen. G.l.c. analysis showed the water content to be <0.1% (w/w). Tetramethylammonium hydroxide was available as the pentahydrate and stock solutions were standardised against potassium hydrogen phthalate. The fluorenes<sup>14</sup> were subjected to vacuum sublimation prior to use. The tritiated compounds were prepared by a method similar to that used for other carbon acids.<sup>4</sup> Doubly deionised, freshly boiled-out water was used throughout the work.

**Kinetics.**—The detritiation technique was the same as that described previously with the difference that because of the observation of a complicating side-reaction with oxygen the solutions had to be vigorously degassed and a stream of nitrogen kept over the surface of the solution. Reactions were followed to at least 80% completion and the pseudo-first-order rate constants ( $k_{\text{obs}}^{\text{T}}$ ) derived from the slopes ( $-k_{\text{obs}}^{\text{T}}/2.303$ ) of the  $\log$  (cts/min) against time plots were reproducible to within  $\pm 2-3\%$ .  $H_-$  Solutions comprising DMSO, H<sub>2</sub>O, and tetramethylammonium hydroxide were made up by weight.

### RESULTS AND DISCUSSION

The rates of detritiation of the three fluorenes (Table I) when plotted in the form of a  $\log k_{\text{obs}}^{\text{T}}$  vs.  $H_-$  correlation (Figure) show that good linear relationships are observed. Only in the case of the most reactive compound, 9-phenylfluorene, which was studied in the least basic and consequently the more aqueous media, is there some sign of scatter in the results. These findings can probably be attributed to the very low solubility of the com-

<sup>9</sup> L. Melander and N. A. Bergman, *Acta Chem. Scand.*, 1971, **25**, 2264.

<sup>10</sup> Z. Margolin and F. A. Long, *J. Amer. Chem. Soc.*, 1972, **94**, 5108.

<sup>11</sup> Z. Margolin and F. A. Long, *J. Amer. Chem. Soc.*, 1973, **95**, 2757.

<sup>12</sup> R. P. Bell and B. G. Cox, *J. Chem. Soc. (B)*, 1971, 783.

<sup>13</sup> K. Bowden and R. S. Cook, *J.C.S. Perkin II*, 1972, 1407.

<sup>14</sup> K. Bowden and A. F. Cockerill, *J. Chem. Soc. (B)*, 1970, 173.

<sup>15</sup> A. Streitwieser, jun., W. B. Hollyhead, G. Sonnichsen, A. H. Pudjaatmaka, P. H. Owens, T. L. Kruger, P. A. Rubenstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. N. Niemeyer, *J. Amer. Chem. Soc.*, 1971, **93**, 5088.

<sup>16</sup> R. A. More O'Ferrall, *J.C.S. Perkin II*, 1972, 976.

<sup>17</sup> D. W. Earls, Ph.D. Thesis, University of Surrey, 1972.

<sup>1</sup> D. Dolman and R. Stewart, *Canad. J. Chem.*, 1967, **45**, 911.

<sup>2</sup> J. R. Jones, *Progr. Phys. Org. Chem.*, 1972, **9**, 241.

<sup>3</sup> E. A. Symons and E. Buncel, *J. Amer. Chem. Soc.*, 1972, **94**, 3641; *Canad. J. Chem.*, 1973, **51**, 1673.

<sup>4</sup> J. R. Jones and R. Stewart, *J. Chem. Soc. (B)*, 1967, 1173.

<sup>5</sup> D. W. Earls, J. R. Jones, and T. G. Rumney, *J.C.S. Faraday I*, 1972, 925.

<sup>6</sup> R. P. Bell and B. G. Cox, *J. Chem. Soc. (B)*, 1970, 194.

<sup>7</sup> R. Stewart and J. R. Jones, *J. Amer. Chem. Soc.*, 1967, **89**, 5069; A. Albagli, R. Stewart, and J. R. Jones, *J. Chem. Soc. (B)*, 1970, 1509.

<sup>8</sup> D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfeld, *J. Amer. Chem. Soc.*, 1961, **83**, 3678.

pound in these solutions. Indeed it is precisely this difficulty that has delayed the development of an  $H_-$  scale based on carbon acids that is firmly anchored in aqueous solutions of hydroxide ion.<sup>18</sup>

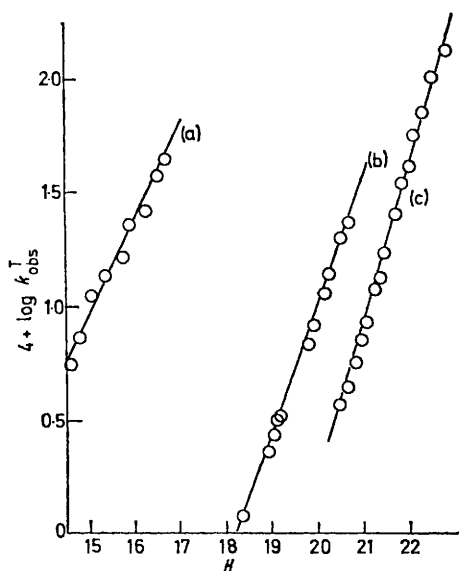
Because of the solubility difficulties and the fact that the rates become very slow in the less basic media so that the likely importance of complicating side-reactions with traces of oxygen is greatly increased no measurements were made in solutions of  $H_- < 14.5$ . It is of course in

The main interest in the  $\log k$  vs.  $H_-$  correlations lies in the magnitude of the slopes. For 9-phenylfluorene the value is  $0.40 \pm 0.01$ , increasing to  $0.56 \pm 0.01$  for fluorene and  $0.74 \pm 0.01$  for 9-t-butylfluorene. This trend of increasing slope with decreasing acidity is in keeping with the results of other studies (Table 2). Thus for DMSO the weakest acid studied, the slope is 0.93; 2-methyl-3-phenylpropionitrile, an acid of similar strength gives a slope of just over unity when studied in

TABLE 1  
Rate constants for the detritiation of fluorene-type carbon acids in aqueous dimethyl sulphoxide containing tetramethylammonium hydroxide (0.010M) at 298 K together with  $H_-$  values

9-t-Butylfluorene								
Mole % Me <sub>2</sub> SO	79.0	80.2	82.1	82.8	83.8	85.4	86.3	87.0
$H_-$	20.48	20.63	20.85	20.94	21.06	21.25	21.36	21.45
$10^4 k_{\text{obs}}^T / \text{s}^{-1}$	3.76	4.42	5.70	7.11	8.49	12.0	13.4	17.0
Fluorene								
Mole % Me <sub>2</sub> SO	88.8	89.8	90.05	91.2	91.9	92.6	93.5	
$H_-$	21.70	21.85	21.97	22.10	22.30	22.50	22.65	
$10^4 k_{\text{obs}}^T / \text{s}^{-1}$	25.2	34.5	40.9	55.9	70.3	101	132	
9-Phenylfluorene								
Mole % Me <sub>2</sub> SO	58.5	64.0	65.1	66.4	72.0	72.9	76.1	77.0
$H_-$	18.35	18.91	19.02	19.15	19.72	19.82	20.16	20.26
$10^4 k_{\text{obs}}^T / \text{s}^{-1}$	1.09	2.31	2.75	3.26	6.84	8.36	11.4	13.8
Mole % Me <sub>2</sub> SO	79.1	80.6	82.5					
$H_-$	20.50	20.67	29.9					
$10^4 k_{\text{obs}}^T / \text{s}^{-1}$	20.0	23.6	28.9					
Mole % Me <sub>2</sub> SO	21.3	23.0	25.5	28.2	32.2	34.0	37.6	40.2
$H_-$	14.61	14.80	15.06	15.34	15.73	15.90	16.25	16.51
$10^4 k_{\text{obs}}^T / \text{s}^{-1}$	5.61	7.41	11.2	13.8	16.6	22.9	26.3	37.6
Mole % Me <sub>2</sub> SO	42.2							
$H_-$	16.70							
$10^4 k_{\text{obs}}^T / \text{s}^{-1}$	44.3							

this region that differences in activity coefficient behaviour between the fluorenes and the nitrogen acids employed in setting up the  $H_-$  scale might be expected



Plot of logarithm of detritiation rate constant ( $k_{\text{obs}}^T$ ) against the  $H_-$  values of the medium: (a) 9-phenylfluorene; (b) fluorene; (c) 9-t-butylfluorene

to be at their maximum and it is precisely in this region that deviations from linearity in  $\log k$  vs.  $H_-$  correlations have been observed.<sup>4-6</sup>

DMSO-MeOH-OMe.<sup>9</sup> On the other hand the three carbon acids activated by a carbonyl group and of probably closely similar acid strengths [(–)-menthone, 2-phenylpropiophenone, and acetophenone] all give very similar slopes close to 0.5. Although the acidities of

TABLE 2 Slopes of $\log k$ vs. $H_-$ correlations for various carbon acids*			
Carbon acid	$pK_a$	Slope	Ref.
9-Phenylfluorene	18.5	0.40	Present work
Fluorene	22.1	0.56	Present work
9-t-Butylfluorene	23.4	0.74	Present work
Acetophenone	21.5	0.47	4
2-Phenylpropiophenone		0.49	5
(–)-Menthone	~21	0.48	6
Chloroform		0.98	11
1,4-Dicyanobut-2-ene	~21	0.71	10
Nitroethane	8.6	0.72	12
DMSO	~32	0.93	7

\* All results refer to DMSO-OH<sup>-</sup>-H<sub>2</sub>O.

several of the compounds in these highly basic solutions are not known with great certainty it seems clear that the behaviour of the fluorenes is not unlike that of the ketones. On the other hand nitroethane and chloroform do not conform to this pattern as the magnitude of the slopes are higher than expected. It is interesting to

<sup>18</sup> A. F. Cockerill and J. D. Lamper, *J. Chem. Soc. (B)*, 1971, 503.

note that these two reflect the extremes of behaviour witnessed on undergoing ionisation; in the case of chloroform the negative charge is well concentrated on the carbon atom and structural modification is at a minimum, whereas for nitroethane the anion is considerably stabilised by rearrangement and the negative charge now resides on oxygen.

The exact significance to be attached to the magnitude of the slopes is difficult to assess. In theory it would be preferable to plot the  $\log k_{\text{obs}}^T$  values against the  $H_-$  of the solutions as obtained using fluorene indicators. This results in a decrease in the magnitude of the slopes, *e.g.* for 9-phenylfluorene from 0.40 to 0.25. However this scale is not as firmly based as that set up by Dolman and Stewart<sup>1</sup> using nitrogen indicators and furthermore only caters for 75% of the solvent variation for water-DMSO mixtures. At present therefore it seems best to compare the rate accelerations with the nitrogen-based  $H_-$  scale. Then by analogy with the Brønsted equation relating kinetic and equilibrium acidities, increasingly positive values of the slopes may be taken to signify an increasing resemblance between the transition state of the reaction and the products.

<sup>19</sup> A. Stretwieser, jun., W. B. Hollyhead, G. Sonnichsen, A. H. Pudjaatmaka, C. J. Chang, and T. L. Kruger, *J. Amer. Chem. Soc.*, 1971, **93**, 5096.

Further evidence, which at least qualitatively supports this interpretation is available. Thus in the case of DMSO the reverse reaction, protonation of the dimethyl anion, is likely to be either diffusion controlled or very close to diffusion control so that the proton in the transition state is very close to the hydroxide ion. Secondly, two separate studies<sup>19,20</sup> show that the enthalpy of activation for the detritiation reaction increases considerably as the acidity of the carbon acid decreases, in line with Hammond's postulate that for highly endothermic reactions, the transition state resembles the products. Finally several recent studies on the variation of primary kinetic hydrogen isotope effects<sup>5,6,9,12</sup> with  $H_-$  provide information entirely consistent with the  $\log k$  vs.  $H_-$  relationships, the only difference being that this method is a still more sensitive probe of transition state structure. In other words whilst the slope of the  $\log k$  vs.  $H_-$  relationship remains constant,  $k^H/k^T$  varies in a regular manner.

Support from the S.R.C. (to T. G. R.) and the University of Surrey (D. W. E.) is gratefully acknowledged.

[4/1339 Received, 3rd July, 1974]

<sup>20</sup> A. Albagli, J. R. Jones, and R. Stewart, *Canad. J. Chem.*, 1974, **52**, 1059.