Diradical Wells, X[≠]

Thermochemistry of 7,7-Difluoro-2,7-toluenediyl

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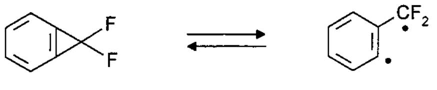
From the oxygen and temperature dependence of the trapping rate of 7,7-difluorobenzocyclopropene (**1**) in the range 180–240 °C, the energy profile of the equilibrium **1** $\rightleftarrows$ **2** has been obtained. From the heat of hydrogenation of **1**, its heat of formation is derived (ΔH_f^o = +3.8 kcal·mol^{-1}), as a result of which the heat of formation of the singlet state of the diradical **2** is estimated as 25.7 kcal·mol^{-1}. Whereas the trapping experiments demonstrate unambiguously a triplet ground state for **2**, only a lower limit for the singlet-triplet splitting (> 6 kcal·mol^{-1}) can be given.

Introduction

In 1994, Squires et al.[2] reported on a determination of the heat of formation of α,2-dehydrotoluene by the CID method. However, the experimental value did not agree well with that calculated by ab initio methods.

We have now analyzed the equilibrium of 7,7-difluorobenzocyclopropene (**1**) with 7,7-difluoro-2,7-toluenediyl (**2**) (Figure 1) so as to get a reliable heat of formation value for the difluoro derivative of the diradical studied by Squires.



1 **2**

Figure 1

The starting point for our investigation was the report of Closs,[3] who established the equilibrium of benzocyclopropenes with α,2-dehydrotoluenes. Because of its ease of dimerization,[4] the parent system is not suitable for studying this equilibrium. In contrast to other 7,7-disubstituted derivatives,[4] 7,7-difluorobenzocyclopropene[5] proved to be extremely stable. It can be heated in the gas phase up to 400 °C without any decomposition.

In the presence of oxygen, the disappearance of the substrate is observed at temperatures > 170 °C and follows strictly first-order kinetics. The reaction was monitored at four different temperatures (180−240 °C), each at five different oxygen concentrations (3×10^{-3} to 6×10^{-5} mol·L^{-1}). The rates of disappearance are listed in Table 1 and their dependence on the oxygen concentration is shown graphically in Figure 2.

As is indicated by the nonlinear curve in Figure 2, the consumption of **1** is due to the trapping of a compound formed in a pre-equilibrium. With regard to the results of Closs,[3] it is reasonable to assume that the mechanism shown in Scheme 1 is in operation. The rate should then be described by Equation (1).

$$k_{dis} = k_{1,2S} \bullet \left(1 - \frac{k_{2S,1}}{k_{2S,1} + k_{2S,2T} + k_s \bullet [O_2] - \dfrac{k_{2S,2T} \bullet k_{2T,2S}}{k_{2T,2S} + k_s \bullet [O_2]}} \right) s^{-1} \qquad (1)$$

At high oxygen concentrations, the decrease approaches asymptotically a limiting value, which describes the situation where all diradicals are trapped and the rate becomes identical to $k_{\mathbf{1,2S}}$. At low concentrations of the trapping reagent, the trapping curve is almost linear and its extrapolation shows an intercept characteristic for diradicals having a triplet ground state.[6] As a result of the large singlet-triplet splitting, the triplet diradicals are trapped quantitatively, even at very low oxygen concentrations, giving rise to a sudden fall off of the trapping curve. At higher oxygen concentrations, when all triplet-diradicals are trapped, the triplet contribution to the trapping curve is limited by the ISC rate $k_{\mathbf{2S,2T}}$, and has no further effect on the slope of the curve. To extract values for $k_{\mathbf{2S,1}}$, $k_{\mathbf{2S,2T}}$ and $k_{\mathbf{2T,2S}}$ from the trapping curve in Figure 2, k_s, the rate at which the diradical reacts with oxygen, has to be known. It has been shown repeatedly[1] that diradicals react with oxygen in a collision-controlled fashion, and k_s can therefore be equated to 5.5×10^8 s^{-1}.[7] Though the absolute value of the rate constant k_s is thus not known with high accuracy, it does not affect the calculated activation enthalpy. Since k_s represents a collision-controlled reaction, its temperature dependence follows a $T^{1/2}$ law, and only this relation enters the calculation of the activation enthalpy. The uncertainty in k_s on the other hand shows up only in the A-factor of the reaction.

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Table 1. Activation parameters

Substrate	Titration rate[a]	Amount of catalyst[b]	H_2 consumed[c]	Energy[d]	$-\Delta H_H$[e]	$-\Delta H_H$[e]
1	0.4657	0.1051	0.19084	6.2228	132.43	
1	0.4532	0.4981	0.18757	6.1935	132.08	
1	0.3493	0.0334	0.13219	4.3827	132.62	
1	0.3493	0.0531	0.14235	4.6639	131.05	
						132.0 ± 0.3

[a] [mol·s^{-1}·10^7]. – [b] [g]. – [c] [mol·s^{-1}·10^6]. – [d] [mcal·s^{-1}]. – [e] [kcal·mol^{-1}].

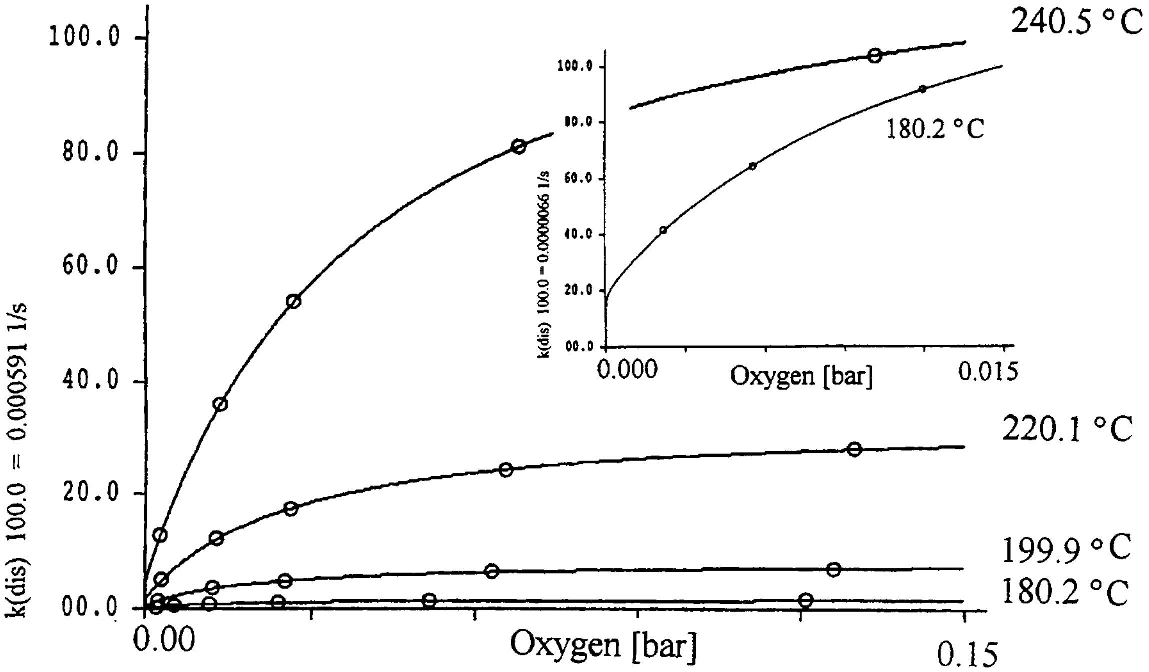
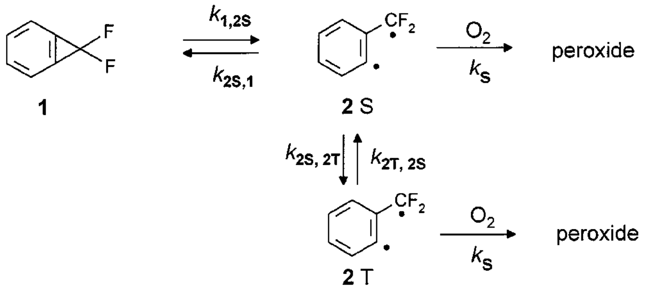


Figure 2. Oxygen dependence of the rate of disappearance of **1**



Scheme 1. Mechanism for the trapping reaction of **1**

The evaluation of the data in Table 1 was performed by simulation of the reactions shown in Scheme 1 and fitting $k_{1,2S}$, $k_{2S,1}$, $k_{2S,2T}$ and $k_{2T,2S}$ to these data by a simplex routine.[8] The resulting activation parameters are collected in Table 2. Whereas $k_{1,2S}$, $k_{2S,1}$ and $k_{2S,2T}$ could be obtained with reasonable uncertainty limits ($k_{1,2S}$ is given by the plateau at high oxygen concentration, $k_{2S,1}$ by the slope of the trapping curve at low oxygen concentration, and $k_{2S,2T}$ by the intercept of the extrapolated trapping curve), this was not the case for $k_{2T,2S}$. This rate is determined from the fall off of the trapping curve at very low oxygen concentrations. In this region we do not have sufficient experimental points

Table 2. Rate constants for the disappearance of **1** in the presence of oxygen

Temp [°C]	180.21	180.35	180.23	180.29	180.21	180.24
$[O_2] \cdot 10^4$ mol · l^{-1}	0.5984	1.4730	3.1834	6.4392	13.771	31.116
$k_{dis} \cdot 10^6$ [s^{-1}]	3.8696	4.5562	5.9464	8.9221	10.210	11.429

Temp [°C]	199.90	199.92	199.95	199.96	200.09
$[O_2] \cdot 10^4$ mol · l^{-1}	0.6648	3.1894	6.4397	16.085	32.087
$k_{dis} \cdot 10^5$ [s^{-1}]	1.1253	2.2519	3.0711	4.2408	4.6598

Temp [°C]	220.14	220.12	220.10	220.07	220.08
$[O_2] \cdot 10^4$ mol · l^{-1}	0.7624	3.1922	6.4009	15.968	31.616
$k_{dis} \cdot 10^5$ [s^{-1}]	3.1751	7.3378	10.087	14.427	16.874

Temp [°C]	240.51	240.47	240.54	240.63	240.57
$[O_2] \cdot 10^4$ mol · l^{-1}	0.6289	3.1677	6.2888	15.895	31.263
$k_{dis} \cdot 10^5$ [s^{-1}]	7.5077	21.435	32.181	48.000	57.797

and hence the given activation energy E_a (**2**T, **2**S) = 6 kcal·mol^{-1} is only a lower limit.

Using the activation enthalpies given in Table 2, the heat of formation of the diradical **2** can be related to the heat of formation of benzocyclopropene **1**. To obtain the latter parameter we carried out heat of hydrogenation measurements,[9] through which the heat of formation of **1** could be linked to that of 1,1-difluorocycloheptane (**3**), the sole product obtained upon catalytic hydrogenation (Pd/C in isooctane) of **1**. The heat of formation of **3** can be derived from the heat of formation of cycloheptane (**4**) by correction for the increment of the CF_2 group:ΔH_f^o = −28.21 (cycloheptane)[10] + {4.93 [$C-(H)_2(C)_2$][11] + −104.9 [$C-(F)_2(C)_2$][12]} = −128.18 kcal·mol^{-1}

Table 3. Data for the heat of hydrogenation measurements[18]

Reaction	T_m[a]	E_a[b][c]	log A[b]	$\Delta H^\ddagger$[b][c]	$\Delta S^\ddagger$[b][d]
$k_{\mathbf{1},\mathbf{2}S}$	210	31.3 ± 0.2	10.15 ± 0.06	30.3 ± 0.2	−15.05 ± 0.25
$k_{\mathbf{2}S,\mathbf{1}}$	210	9.3 ± 0.5	11.13 ± 0.23	8.4 ± 0.5	−10.55 ± 1.05
$k_{\mathbf{2}S,\ \mathbf{2}T}$	210	0.1 ± 0.2	7.2 ± 0.1		
$k_{\mathbf{2}T,\ \mathbf{2}S}$	210	> 6	8		

[a] [°C]. – [b] Uncertainty limits are based on a 95% confidence level and have been calculated for data obtained by simulation using the method of Nelder.[17] – [c] [kcal·mol^{-1}]. – [d] [cal·K^{-1} mol^{-1}].

Using a value of ΔH_H = 132.0 kcal·mol^{-1} for the heat of hydrogenation (Table 3), one obtains for the heat of formation of **1** ΔH_f^o = + 3.8 kcal·mol^{-1}. From the enthalpy profile for the equilibrium **1** ⇄ **2** shown in Figure 3, a heat of formation for the singlet state of the diradical **2** of ΔH_f^o = 25.7 kcal·mol^{-1} can then be obtained.

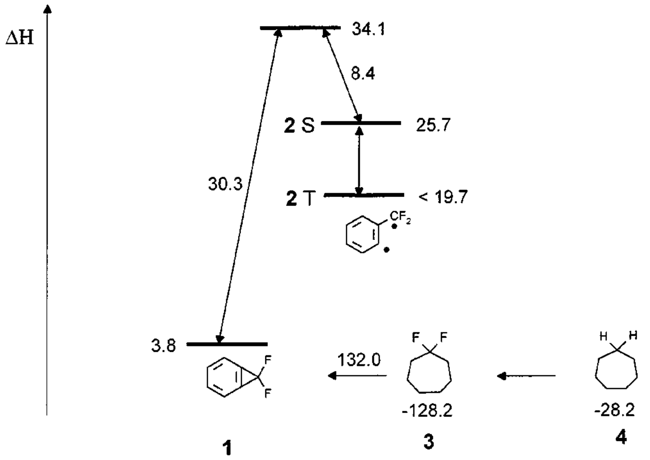
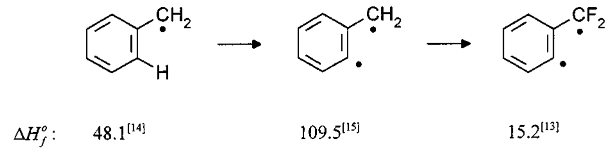


Figure 3. Enthalpy profile [kcal·mol^{-1}] for the equilibrium **1** ⇄ **2**

According to the trapping kinetics, the diradical **2** has a triplet ground state, which is in agreement with findings for other α,2-toluenediyls.[3] The heat of formation for the singlet state can be considered as being highly reliable because of the accurate activation parameters for $k_{\mathbf{1},\mathbf{2}S}$ and $k_{\mathbf{2}S,\mathbf{1}}$. The heat of formation of the triplet state, however, is only an upper limit, which gives the singlet-triplet splitting as > 6 kcal·mol^{-1}. For the parent system, Squires[2] calculated a value of 7.4 kcal·mol^{-1}.

In the triplet-state, no interaction between the unpaired electrons should occur. Its heat of formation, therefore, should also be accessible by the abstraction of two hydrogen atoms from 7,7-difluorotoluene. The dissociation energy required for each step should correspond to the energy needed to generate the equivalent monoradical. Starting from the known heat of formation of the benzyl radical,[13] the abstraction of the phenyl hydrogen at C^2 [14] yields a diradical, which can be transformed to the diradical **2** by the functional group increments published by Dolbier[12] (Scheme 2). The resulting heat of formation of ΔH_f^o = 15.2 kcal·mol^{-1} should be compared to the upper limit of ΔH_f^o (**2**T) derived from the kinetic measurements (ΔH_f^o = <19.7 kcal·mol^{-1}).



Scheme 2. Heat of formation [kcal·mol^{-1}] of the noninteracting diradical **2**

As a 1,3-diradical, the recombination enthalpy of **2**S of 8.4 kcal·mol^{-1} is unusually large, and, together with the low A-factor, this indicates that the ring closure necessitates rotation of the CF_2 group. In the singlet- as well as in the triplet-state of the diradical, the CF_2 group seems therefore to be oriented parallel to the phenyl ring, so that the singlet-state is best described by the carbene-like structure **2b**, whereas the triplet-state should have the structure **2a** (Figure 4).

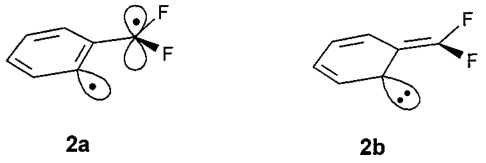


Figure 4

Experimental Section

Kinetic Measurements: The rate constants listed in Table 1 were measured using techniques and apparatus described previously.[15]

Heat of Hydrogenation Measurements: The calorimeter and method used, as well as an assessment of the degree of accuracy, have been described previously.[9] The data from the individual runs are collected in Table 3. The hydrogenation was carried out at 25 °C in isooctane, using 10% Pd/C as the catalyst. The values are not corrected for evaporation effects, but for effects of the solvent according to the literature.[16] The hydrogen uptake was used for the analyses.

Acknowledgments

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