Relative Reactivities of Styrene, α,β,β-Trifluorostyrene and Phenylacetylene toward Attacks of Trichloromethyl Radicals as measured by Direct Competition between the Substrates

J. Chem. Research (S),
1997, 6–7
J. Chem. Research (M),
1997, 0139–0151

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The relative rates of the addition of trichloromethyl radicals to styrene, α,β,β-trifluorostyrene and phenylacetylene in cyclohexane at 65 °C, measured by a direct competition procedure, are 1 : 0.23 : 0.40.

The π-bond dissociation energy of tetrafluoroethylene may be *ca*. 30 kJ mol^{-1} less than that of ethylene,[1] possibly because of the p–π repulsion between the unshared p-electron pair of the α-positioned fluorine atoms and the π electrons of the double bond in $CF_2{=}CF_2$.[2] Thus a relatively 'neutral' radical that is neither distinctly nucleophilic nor electrophilic, such as the methyl radical, has been found to add to $CF_2{=}CF_2$ ten times faster than to $CH_2{=}CH_2$.[4a] Also, for the cyclodimerization reaction, the activation energy for $CF_2{=}CF_2$ is *ca*. 82 kJ mol^{-1} less than that for $CH_2{=}CH_2$. On the other hand, it has been well established that polar effects play an important role in radical additions to olefins.[4] For illustration, $CF_2{=}CF_2$ is less reactive than $CH_2{=}CH_2$ for additions by electrophilic radicals.[4a] Therefore, it would be of great interest to know the relative reactivity of styrene (**1**) and α,β,β-trifluorostyrene (**2**). Furthermore, although the carbon–carbon triple bond is generally known to be less reactive than the carbon–carbon double bond toward electrophilic radical addition, $CF_2{=}CF_2$ was reported to be less reactive than $CH{\equiv}CH$.[8] Thus it would also be worthwhile to measure the relative reactivity of α,β,β-trifluorostyrene (**2**) and phenylacetylene (**3**). Various techniques involving kinetic competition with a standard substrate have been extensively used.[9–13] Relative rates [k_r(**2**/**1**)] of two substrates attacked by the same radical can also be evaluated by measuring the relative conversions of the two competing substrates, *i.e.*, substrate **1** (with substituent Y_1) and substrate **2** (with substituent Y_2). As long as the products are derived from the same irreversible elementary step, the relative rate k_r can be calculated by the well established eqn. (1),[9] in which φ is defined as the mole fraction of the unreacted substrate, *i.e.* $[\mathbf{1}]_t/[\mathbf{1}]_0$ or $[\mathbf{2}]_t/[\mathbf{2}]_0$. Recently, we have developed a rigorous experimental procedure for the application of eqn. (1),

$Ph\,CR{=}CR_2$ $Ph\,CR{\equiv}CH$
1 R = H **3**
2 R = F

$$k_r(\mathbf{2}/\mathbf{1}) = \frac{\log\{[\mathbf{2}]_t/[\mathbf{2}]_0\}}{\log\{[\mathbf{1}]_t/[\mathbf{1}]_0\}} = \frac{\log\varphi_2}{\log\varphi_1} \qquad (1)$$

i.e., we require the measurement of at least five independent k_r values over a wide range of the extent of the reaction, *e.g.*, from 5–10% to 75–90% conversion. The reliability of the measured relative rates and the cleanness of the reactions can be assessed from the value of the correlation coefficients (r values) of the regression analysis of the $\ln\varphi_2$ *vs.* $\ln\varphi_1$ straight-line plot based on the φ values measured at different time intervals. This method has been successfully applied to measurement of the relative rates of radical reactions of substrates with different substituents, with r values falling in the range 0.990–0.999.[14] The present work is the first attempt to apply our rigorous methodology to the determination of the relative reactivities of different types of substrates by their direct competition. With trichloromethyl radicals as the addendum radicals,[14a,d] the substrates are the phenyl-substituted ethylene, tetrafluoroethylene and acetylene, *i.e.*, styrene (**1**), α,β,β-trifluorostyrene (**2**) and phenylacetylene (**3**).

A cyclohexane (5 ml) solution of styrene (0.2 mmol), α,β,β-trifluorostyrene[16] (0.2 mmol), CCl_3SO_2Br (1.2 mmol) and internal GC standards [$C_{14}H_{30}$ (10 μl); $C_{15}H_{32}$ (16 μl)] was stirred at 65 ± 0.5 °C for 2 h. GC analyses at seven consecutive time intervals gave six values based on the independently measured $\ln\varphi_2/\ln\varphi_1$ ratios. The first tube taken at time zero gave no k_2/k_1 value, but it served as a standard for $\varphi_2 = 1$ and $\varphi_1 = 1$. These six k_2/k_1 values were the same within experimental error (± 0.01). In a plot of $\ln\varphi_2$ *vs.* $\ln\varphi_1$, regression analysis of the straight line (see Fig. 1) gave the slope, *i.e.*, a k_r(**2**/**1**) value of 0.23 ± 0.01 (Table 2). This is the same as the k_{av}(**2**/**1**) value obtained by simply averaging the six independently measured k_2/k_1 values mentioned above.

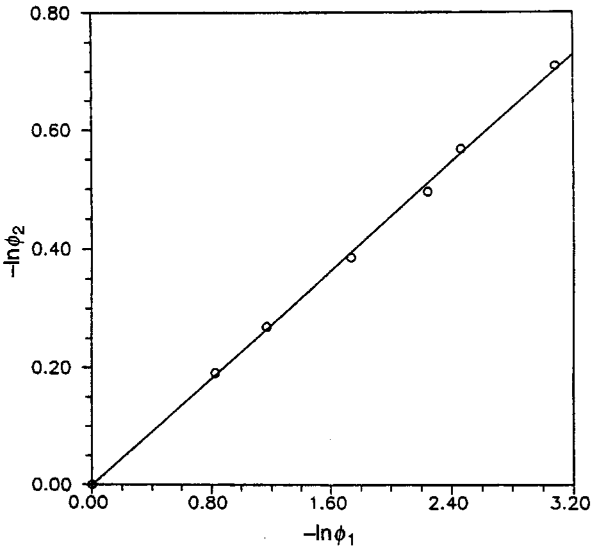

Fig. 1 Plot of $(-\ln\varphi_s)$ *vs.* $(-\ln\varphi_1)$

Table 2 Relative rates of α,β,β-trifluorostyrene (**2**), styrene (**1**) and phenylacetylene (**3**) towards attacks by $CCl_3\cdot$ radicals in cyclohexane at 65 °C

Substrates	Ratio	$k_r \pm \Delta k_r$[a]	r	$k_{av} \pm \Delta k_{av}$[b]
2/1	1:1	0.22 ± 0.01, $n = 7$	0.9984	0.22 ± 0.01, $n = 6$
	5:1	0.23 ± 0.01, $n = 7$	0.9994	0.23 ± 0.01, $n = 6$
2/3	1:1	0.58 ± 0.02, $n = 6$	0.9950	0.58 ± 0.02, $n = 5$
3/1[c]		0.40 ± 0.03		0.40 ± 0.03

[a] k_r is the relative rate obtained from the regression line of $(-\ln\varphi_2$ *vs.* $-\ln\varphi_1)$.
[b] k_{av} is the arithmetically averaged relative rate ratios (k_2/k_1 at time t).
[c] k_r (or k_{av}) (**3/1**) $= k_r(\mathbf{2/1})/k_r(\mathbf{2/3})$, Δk_r (or Δk_{av}) (**3/1**) $= \Delta k_r(\mathbf{2/1})/k_r(\mathbf{2/3}) + \Delta k_r(\mathbf{2/3})\cdot k_r(\mathbf{2/1})/k_r^2(\mathbf{2/3})$.

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Furthermore, the $k_r(\mathbf{2}/\mathbf{1})$ values were found to be independent of the molar ratios of **1** and **2** (1:1 and 5:1).

Direct composition of styrene (**1**) with phenylacetylene (**3**) could not be carried out because the retention times of these substrates under our GC conditions are almost the same. However, the relative rate of α,β,β-trifluorostyrene (**2**) and phenylacetylene (**3**) could be measured at a **2**:**3**:CCl_3SO_2Br molar ratio of 1:1:6. The solution was stirred at 65 °C for 8 h, six samples were withdrawn and analysed, and the k_r values are listed in Table 2. These show that the regression slope $[k_r(\mathbf{2}/\mathbf{3}) = 0.58 \pm 0.02]$ is also the same as the averaged value of five independently measured k_2/k_3 values, whereupon the relative reactivity of styrene (**1**) and phenylacetylene (**3**) can be calculated $[k_r(\mathbf{3}/\mathbf{1}) = k_r(\mathbf{2}/\mathbf{1})/k_r(\mathbf{2}/\mathbf{3}) = (0.21 \pm 0.01)/(0.58 \pm 0.02) = 0.40 \pm 0.03$, see Table 2]. All these results demonstrate that our methodology for the determination of the relative reactivity of two substrates by direct competition for a common attacking radical is reliable and trustworthy.

The above-mentioned experiments are first attempts to measure the relative reactivities of styrene (**1**), α,β,β-trifluorostyrene (**2**) and phenylacetylene (**3**) by direct competition between the substrates. The relative reactivities of **1**, **2** and **3** toward $CCl_3\cdot$ radicals are found to be 1:0.23:0.40. The reactions of styrene and phenylacetylene with CCl_3SO_2Br have previously been proved to be very clean radical-chain reactions with truly free $CCl_3\cdot$ radicals as chain carries,[14a,d] and the reaction of $\alpha,\beta\beta$-trifluorostyrene with CCl_3SO_2Br is expected to follow the same mechanistic path. This expectation is supported by the following facts: (1) although cyclodimerization of **2** could be a possible side-reaction, no cyclodimerization products, *i.e.*, *cis*- and *trans*-1,2-diphenylhexafluorocyclobutane,[15a] could be detected by GC under our experimental conditions; (2) the constancy (within experimental uncertainty) of our six k_2/k_1 values measured at six time intervals (Fig. 1). In short, our measurements truly reflect the relative reactivities of **1**, **2** and **3** towards $CCl_3\cdot$ radicals. The relative reactivity of **1** and **3** towards $CF_3\cdot$ radicals at 65 °C can be assessed to be roughly 1:0.30,[8,10] which is comparable with the relative reactivity of **1** and **3** towards $CCl_3\cdot$ radicals (1:0.40) found in this work.

The D_π of α,β,β-trifluorostyrene is expected to be lower than the D_π of styrene because (1) the D_π of $CF_2{=}CF_2$ is lower than the D_π of $CH_2{=}CH_2$, and (2) cyclodimerization of α,β,β-trifluorostyrene occurs readily at temperatures above 110 °C,[15a] whereas cyclodimerization of styrene does not take place. Therefore, for the attacks by radicals which are neither electrophilic nor nucleophilic, the reactivity of trifluorostyrene should be greater than that of styrene. However, for electrophilc radicals such as $CCl_3\cdot$, the reactions are affected by the polar effects as well as by the D_π values of the substrates. Consequently, styrene is more reactive towards electrophilic $CCl_3\cdot$ than is α,β,β-trifluorostyrene because of the operation of sizeable polar effects. Furthermore, although the reactivity of styrene is expected and found to be greater than that of phenylacetylene, the fact that α,β,β-trifluorostyrene is found to be less reactive than phenylacetylene further demonstrates that polar effects play an important role in radical addition reactions.

We gratefully acknowledge financial support by the National Natural Science Foundation of China.

Techniques used: ^1H NMR, MS, ^{19}F NMR, GC

References: 19

Figure: 1

Table 1: φ Values for the reaction of **2** and **1** in competition for $CCl_3\cdot$ radicals at seven successive time intervals

Received, 28th May 1996; Accepted, 7th October 1996
Paper E/6/03665A

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