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Absolute Rate Constants of Alkene Addition Reactions of a Fluorinated Radical in Water

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Abstract: Absolute rate constants of $\cdot R_fSO_3^-$ radical addition to a series of water-soluble alkenes containing ionic, carboxylate substituents were measured by laser flash photolysis experiments in water. The observed rate constants were all considerably larger than those of structurally similar analogues in a nonpolar organic solvent, with rate factors of 3−9-fold being observed. It is concluded that such rate enhancements derive at least in part from stabilization of the polar transition state for addition of the electrophilic fluorinated radical to alkenes by the polar solvent water.

Introduction

Over the past decade, we have been engaged in a broad investigation of structure−activity relationships in the alkene addition and hydrogen abstraction reactions of fluorinated radicals,[1−3] including, most recently, a study of the absolute rate constants of H atom abstraction from organic compounds.[4] However, until now, little attention has been paid to the influence of solvent on these reactions. Because of their high electrophilicities and the acknowledged importance of transition state polar effects on their reactivities in both hydrogen abstraction and alkene addition reactions,[3] one would predict that the rates of such reactions of perfluoro-*n*-alkyl radicals would be influenced by solvent polarity.[5]

Minor mention of solvent effects (in a footnote) was made in one of our earlier LFP studies of alkene addition reactions of $CF_3\cdot$ and n-$C_3F_7\cdot$ radicals.[6] Thus, both radicals were found to add to styrene ∼3 times faster in CH_3CN compared to 1,1,2-trichloro-1,2,2-trifluoroethane (F113), whereas the rate factor was only ∼1.5 for their additions to the less nucleophilic pentafluorostyrene.

Recently, we initiated a broad investigation to measure the absolute rate constants for the addition and hydrogen atom abstraction reactions of fluorinated radicals in water. Since the rate constants of such reactions in nonpolar organic solvents (F113, C_6D_6, and 1,3-bis(trifluoromethyl)benzene (BTB)) are available,[3,4] insight into the significance of solvent effects on these reactions should be obtained from this study. In this initial paper, we report data from an LFP study of the addition of a fluorinated radical to various alkenes in water.

Results

The addition reactions of perfluoro-*n*-alkyl radicals ($C_2F_5\cdot$, n-$C_3F_7\cdot$, n-$C_7F_{15}\cdot$, and n-$C_8F_{17}\cdot$) to alkenes in nonpolar organic solvents (F113 and C_6D_6) were studied previously, with absolute rate constants being determined by a combination of product analyses, LFP technique, and competition kinetic methods.[1] In these studies, it was demonstrated that transition state polar effects comprised a very important factor in determining the rates of such reactions. The results also showed that perfluoro-*n*-alkyl radicals with at least 3 carbons have essentially the same reactivity.

Synthesis of Water-Soluble Reactants. To study the reactions of a fluorinated radical with alkenes in aqueous solution, it is necessary to use a radical precursor and alkenes that have adequate solubilities in water. None of the radical precursors or alkenes used in previous studies had sufficient solubility in water to allow their use in the current study. Therefore we employed an appropriate, water-soluble perfluoro, carbon-centered radical precursor and new alkene substrates, with structures similar to those used previously in the nonpolar studies.

(a) Water-Soluble Radical Precursor. Sodium 5-iodo-3-oxaoctafluoropentanesulfonate (**1**) ($ICF_2CF_2OCF_2CF_2SO_3Na$) was prepared, as a white solid with a very clean ^{19}F NMR spectrum, by hydrolysis of $ICF_2CF_2OCF_2CF_2SO_2F$ in H_2O. For our kinetic studies, this solid was purified further by recrystallization from water, which provided $ICF_2CF_2OCF_2CF_2SO_3Na\cdot H_2O$ (henceforth abbreviated as $IR_fSO_3^-$) as an analytically pure compound. It has a UV spectrum ($\lambda_{max} = 262$ nm) that extends

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with significant extinction coefficient to above 320 nm and was found to provide sufficient optical density to allow laser flash photolysis at 308 nm.

$$ICF_2CF_2OCF_2CF_2SO_2F + 2NaOH \xrightarrow[\text{overnight, 87\%}]{H_2O,\ 90\ °C} ICF_2CF_2OCF_2CF_2SO_3^-Na^+$$

1

(b) Water-Soluble Alkenes. Five water-soluble styrene type compounds and one terminal alkene were prepared as alkene substrates (Chart 1). The carboxylate functionality was used to make each substrate soluble in water. The $-COO^-Na^+$ group was connected to the benzene ring directly for compounds **2a**−**c**. To determine whether such direct substitution would have any influence on their reactivities toward addition, we also examined the reactivity of **2d**, where the $-COO^-Na^+$ is separated from the phenyl ring by a methylene group. Details related to the syntheses of these alkene substrates may be found in the Supporting Information.

Chart 1. Water-Soluble Alkene Substrates[a,b]

$CH_2{=}CH\text{-}C_6H_4\text{-}CO_2^-\ Na^+$ **2a**

$CH_2{=}C(CH_3)\text{-}C_6H_4\text{-}CO_2^-\ Na^+$ **2b**

$CH_3CH{=}CH\text{-}C_6H_4\text{-}CO_2^-\ Na^+$ **2c**

$CH_2{=}CH\text{-}C_6H_4\text{-}CH_2CO_2^-\ Na^+$ **2d**

$C_6H_5\text{-}CH{=}CH\text{-}CH_2CO_2^-\ Na^+$ **2e**

$CH_2{=}CH\text{-}CH_2CH_2CO_2^-\ Na^+$ **2f**

[a] **2a,b,c,d** are para-substituted. [b] **2c,e** are the trans isomers.

Laser Flash Photolysis Experiments. The $\cdot R_fSO_3^-$ radical was generated "instantaneously" by 308-nm LFP of the parent iodide (ca. 0.03 M)) in water at room temperature, and rate constants for its "global" reactions, k_{gl}, with the five water-soluble styrenes were obtained using standard LFP techniques.[1]

$$k_{exptl} = k_0 + k_{gl}[\text{alkene}] \qquad (1)$$

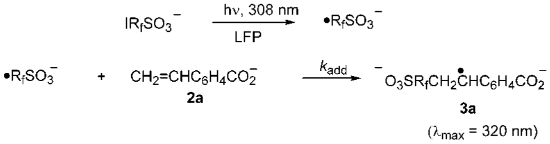
The rate constant for the global reactions of sodium 4-pentenoate (**2f**), which does not form an easily observed radical product, was also measured by LFP at ambient temperature using ca. 0.0019 M sodium 4-(2-propenyl)benzoate (**2c**) as a spectroscopic probe.[1]

$$k_{\mathbf{2f}(exptl)} = k_0 + k_{add(\mathbf{2c})}[\mathbf{2c}] + k_{gl}[\mathbf{2f}] \qquad (2)$$

In separate experiments, the products of these reactions were analyzed quantitatively by ^{19}F NMR, and no $HR_fSO_3^-$ product was observed to be formed, the only products being those of addition to the alkenes.[7] Therefore, it is possible to equate k_{gl} with k_{add} for all the olefins studied.

In typical LFP experiments with **2a** (Scheme 1), pseudo-first-order rate constants (k_{exptl}) for addition of $\cdot R_fSO_3^-$ were obtained at various concentrations of **2a**. Excellent kinetic behavior, with a linear relationship between [**2a**] and k_{exptl}, was observed for the reaction, and a plot of these pseudo-first-order rate constants versus [**2a**] provided the second-order rate constant, k_{add}, as shown in Figure 1.

Scheme 1. Typical LFP Experiment



$$IR_fSO_3^- \xrightarrow[\text{LFP}]{h\nu,\ 308\ nm} \bullet R_fSO_3^-$$

$$\bullet R_fSO_3^- + \underset{\mathbf{2a}}{CH_2{=}CHC_6H_4CO_2^-} \xrightarrow{k_{add}} \underset{\mathbf{3a}}{{}^-O_3SR_fCH_2\dot{C}HC_6H_4CO_2^-}$$

(λ_{max} = 320 nm)

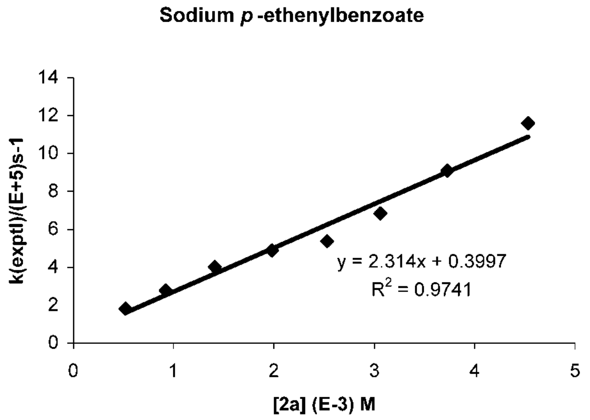
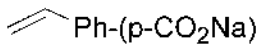
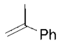
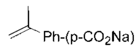
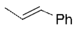
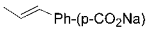
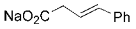
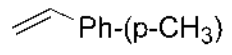
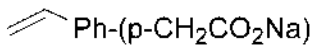
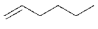
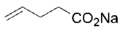


Figure 1. Plot of the pseudo-first-order rate constants, k_{exptl}, vs concentration of **2a**.

Table 1. Absolute Rate Constants for the Addition of $\cdot R_fSO_3^-$ to Six Alkene Substrates at 295 K in H_2O, Measured by LFP

substrate	$k_{add}/10^7\ M^{-1}\ s^{-1}$	rel k_{add}
2a	23.2 ± 0.16	1
2b	55.3 ± 0.25	2.38
2c	3.31 ± 0.28	0.143
2d	20.2 ± 0.13	0.871
2e	1.88 ± 0.11	0.081
2f	2.08 ± 0.26	0.090

Table 2. Comparison of the Rate Constants for Fluorinated Radicals to Alkenes in F113 versus H_2O

	k_{rel}(F113)	$k_{rel}(H_2O)$			$k(H_2O)/k$(F113)
	(1)	(1)		**2a**	5.4
	1.9	2.4		**2b**	7.1
	0.088	0.14		**2c**	8.7
		0.081		**2e**	5.0
	1.3	0.87		**2d**	4.7
	0.14	0.090		**2f**	3.4

The rate constants for addition of $\cdot R_fSO_3^-$ radical to the other styrene substrates (**2b**−**e**) were determined in the same manner, and these rate constants are given in Table 1. Rate constants for the addition of $\cdot R_fSO_3^-$ to $CH_2{=}CHCH_2CH_2COO^-$ (**2f**), were measured by the aforementioned probe technique. In this case a plot of ($k_{exptl} - k_{add(\mathbf{2c})}[\mathbf{2c}]$) versus [**2f**] provided the second-order rate constant for $\cdot R_fSO_3^-$ radical addition to alkene **2f**.

Discussion

In terms of relative rates, the observed trend in reactivities for the series **2a**−**f** in water bears a marked similarity to the trend of reactivities of the $n\text{-}C_3F_7\cdot$ radical in its additions to a similar group of olefins in F113 (Table 2). Thus, an α-methyl substituent gives rise to about a doubling of the rate constant, whereas a *β*-methyl substituent inhibits the addition process (sterically) by approximately a factor of 10. Both nonstyryl,

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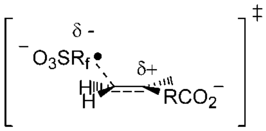
(7) For example, the addition of IR_fSO_2F to 4-pentenoic acid, initiated by AIBN at 80 °C, gave a modest (26%) yield of adduct $FO_2SCF_2CF_2OCF_2CF_2CH_2\text{-}CHICH_2CH_2CO_2H$, which contained only a trace of HR_fSO_2F reduction product. (See Supporting Information.)

terminal alkenes exhibit about 1/10 the reactivity of the respective styrene substrates.

In absolute terms, the rate constants of **2a**−**f** in water are all significantly larger than the rate constants of the most closely analogous alkenes in F113 (Table 2, last column). We believe that the observed rate enhancements in water almost certainly reflect the greater ability of this polar solvent to stabilize the polar transition state for addition of $\cdot R_fSO_3^-$ to the alkenes.

Coulombic Effects. The observed rate enhancements are all the more remarkable in view of the Coulombic repulsion that must be incurred in a transition state such as that below involving two negatively charged ions. It was recognized as early as 1922 by Brönsted that for "ions of the same sign the repulsive forces will tend to keep them apart."[8]



Such electrostatic repulsions should also cause reactions between ions bearing the same charge to be inhibited relative to analogous reactions between neutral species or between a charged and a neutral reactant. A manifestation of this effect is seen in a recent report that demonstrated that pairs of negatively charged radicals in a cage diffuse apart in water much faster (5×) than pairs of neutral radicals.[9]

Hence, in contrast to our actual result, one might have expected that the addition reactions between our negatively charged radical and negatively charged alkene substrates would be *inhibited* by electrostatic repulsion. However, the presence of a polar solvent or a medium of increased ionic strength should at least partially ameliorate the inherently detrimental electrostatic effects present in a reaction between two negatively charged ions and, hence, facilitate such reactions.

Incorporated into the overall "medium" effect that we refer to in this paper as a solvent effect is also the influence of *ionic strength*. According to Debye−Huckel theory, the rate of a reaction between two negatively charged species should be increased in a medium of increased ionic strength. All of the LFP experiments in this study were carried out at a *constant* ionic strength ($I \approx 0.027$). Therefore, the modest, but consistent, ionic strength of our aqueous reaction media will contribute to the overall "medium" effect and have a constant influence upon the magnitude of the observed rate constants in this study. However, the specific kinetic influence of ionic strength has not been evaluated in this investigation.

Other Kinetic Issues. One also needs to consider the possible influence of the carboxylate substituents on the reactivity of the alkene substrates. In this case, the Hammett σ_p values for $-CO_2^-$ and $-CH_2CO_2^-$ are not very helpful. Their respective σ_p values of 0.00 and −0.16 (slightly donating) would predict that **2d** should be slightly more reactive than **2a**, whereas in fact they have almost the same reactivities. Hammett inductive/field constants, *F*, for these substituents (−0.10 and +0.19, respectively) correlate better with the observed slight trend, but all in all, Hammett value consideration would predict only a slight kinetic influence on addition rate constants by either of these substituents. In support of this assertion, the best Hammett correlation for addition of n-$R_f\cdot$ to *p*-substituted styrenes in our earlier studies in F113 was obtained with σ values to give a ρ value of −0.53. This relatively small ρ value indicated that the addition reactions of perfluoro-*n*-alkyl radicals to styrenes are relatively insensitive to the nature of the *p*-substituents. For example, 4-methylstyrene ($\sigma = -0.14$) reacts only 1.3 times faster than styrene. Therefore, although the presence of the slightly donating $-CO_2^-$ substituent on **2a**−**c** might slightly facilitate their addition reaction, such enhancements should not be very large and cannot account for the 5, 7, and 9 times larger rate constants that were observed for **2a**−**c**, respectively. This observed relative insensitivity to substituents should not be surprising in view of the very large, at times almost diffusion-controlled, rate constants observed for these addition reactions (a serious leveling effect).

Another possible issue is the influence on reactivity of the ether oxygen in the $^-O_3SCF_2CF_2OCF_2CF_2\cdot$ radical. Replacement of a $-CF_2-$ group with an oxygen atom at the 3-postion of a perfluoro-*n*-alkyl radical should slightly alter the nature of such a radical to make it more electrophilic, as reflected by the respective inductive/field effects (*F* values) of the $-OCF_2CF_3$ group (0.55) and the $-CF_2CF_2CF_3$ group (0.44). It seems unlikely that such a small difference in *F*-value would lead to a large difference in reactivities between the $^-O_3SCF_2CF_2OCF_2CF_2\cdot$ and n-$R_f\cdot$ radicals.

Although there are no rate data available for a radical of the $R_fOCF_2CF_2\cdot$ type, there are relevant data for the similar radical, $CH_3OCF_2CF_2\cdot$, in F113.[10] This radical exhibited a slightly enhanced reactivity (2.4 and 2.7 times), relative to n-$C_3F_7\cdot$, in its additions to pentafluorostyrene and α-methylstyrene, respectively. However, it had a rate constant for H-abstraction from $(TMS)_3SiH$ that was virtually identical to that for n-$C_3F_7\cdot$, which gives mixed signals regarding the relative electrophilicity of these two radicals. In considering all of the information available, we conclude that the $^-O_3SCF_2CF_2OCF_2CF_2\cdot$ radical should not exhibit an intrinsic reactivity vastly different from that of the n-$R_f\cdot$ radical.

Considering the dilute solutions used in the LFP experiments and the observed linear dependence of k_{exptl} on [alkene], one should be able to rule out aggregation and/or micellar influences on the observed kinetic behavior, and thus our conclusion is that solvent effects provide the simplest and most reasonable explanation for the observed rate constant differences. If not for the negative impact of Coulombic repulsion in the transition state, these rate enhancements would most certainly be much larger.

Further Discussion. Although there is considerable current interest in using water as a medium for carrying out synthetic radical reactions,[11−15] kinetic studies in water remain rare. However, a report last year indicated that triethylborane-induced

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atom transfer radical cyclization reactions proceeded much more effectively in water than in the traditional organic solvents.[16]

In contrast to the relative lack of data in the organic literature, water has long been a popular solvent for carrying out free-radical polymerizations,[17,18] especially of fluorinated monomers.[19] Although most fluoropolymers are now made by dispersion, emulsion, or suspension polymerizations in aqueous media, there are still problems associated with this field that make studies of absolute rates of fluoroalkyl radicals in water of some importance. Undertaking structure−activity relationships for propagation (radical addition) and chain transfer (atom, especially H-transfer) processes of fluorinated radicals will allow fluoropolymer scientists to develop superior initiators and surfactants for polymerization of fluoroolefins and thus allow them to better control the relative rates of propagation and chain transfer and, hence, control the molecular weight of the polymers.[20]

This initial report provides the first absolute rate data for alkene addition processes of a fluorinated radical in water, information which can be related to propagation processes in polymerization of perfluoroolefins. We will soon be reporting the first absolute rate data for H-abstraction processes of this fluorinated radical, the rate constants of which should be related to chain transfer processes in such polymerizations.

Summary

In the current study, absolute rate constants of $\cdot R_fSO_3Na$ radical addition to a series of water-soluble alkenes bearing carboxylate ion functionality in aqueous solution were measured by LFP experiments. As was the case for previous studies in F113 solution, thermodynamic, polar, and steric effects were all observed to be important factors in determining the dynamics of these addition reactions.

With comparison of the relative rates for the series with a similar series that had been studied in F113, it was apparent that steric and thermodynamic factors were similar and essentially independent of the nature of solvent. On the other hand, the rate constants for the series in water, although nearing diffusion control, were all considerably larger than those of their counterparts in F113, with rate factors of 3−9-fold being observed, despite the expected retardation of the additions by Coulombic repulsion. We conclude that these rate enhancements most probably derive from more effective stabilization of the polar transition state for addition of the electrophilic perfluoro-*n*-alkyl radical to alkenes by the polar solvent, water, than by the nonpolar organic solvent, F113.

Experimental Section

Time-Resolved Laser Flash Photolysis. The apparatus and procedures have been described in detail elsewhere.[21,22] The rate constants for the reactions that resulted in the formation of the benzylic radicals were determined from the experimental growth curves of the absorption at ca. 320 nm measured over a range of substrate concentrations, according to eq 1. Rate constants for the alkene that did not form easily observed products were obtained using ca. 0.0019 M sodium 4-(2-propenyl)benzoate (**2c**) as a spectroscopic "probe" according to eq 2.[21]

Preparation of Samples for Laser Flash Photolysis. IR_fSO_3Na (601 mg) was dissolved in 50 mL H_2O to make a 0.027 M stock solution. All the alkene substrate solutions (ca. 0.03 M) were made freshly and used within 1.5 h after being prepared.

Using a pipet, a series of quartz cuvettes were charged with 1.5 mL of the stock solution of IR_fSO_3Na and sealed with rubber septa. They were then degassed by bubbling N_2 through the solution for 10−15 min. During this time, the alkene solution was prepared and degassed by bubbling with N_2 for 20−30 min. Varying portions of alkene solution were then added to the cuvettes using a microliter syringe. The mixtures were shaken well, and they were then, one by one, subjected to laser pulses at 308 nm from an excimer laser, each sample undergoing 7−9 individual flashes in order to obtain an average pseudo-first-order growth curve for generation of the benzylic radicals, which were monitored at ca. 320 nm by UV. The first-order rate constants were obtained from the fitting curve with the best *R* value, and these rate constants were plotted against the concentrations of alkene to give the second-order rate constants

Sodium 5-Iodo-3-oxaoctafluoropentanesulfonate (1). NaOH (2.97 g, 74.1 mmol) was dissolved in 20 mL of H_2O in a 100 mL round-bottom flask equipped with a condenser and stirring bar. To the flask was added tetrafluoro-2-(tetrafluoro-2-iodoethoxy)ethanesulfonyl fluoride ($ICF_2CF_2OCF_2CF_2SO_2F$) (15.8 g, 37.1 mmol). The reaction mixture was stirred overnight at 95 °C. ^{19}F NMR showed the complete consumption of the starting material. The pH of this solution was 7. Vacuum was applied to remove H_2O, giving a solid residue. A 20 mL volume of ethanol was added to the solid to dissolve compound **1**, leaving NaF undissolved. The NaF was removed by filtration, and the filtrate was concentrated on a rotary evaporator to give a white solid residue. After recrystallization from water, the title compound was obtained in 87% yield. Elemental analysis indicated the compound to be $ICF_2CF_2OCF_2CF_2SO_3Na\cdot H_2O$: mp 151 °C, dec; ^{19}F NMR (D_2O/$CFCl_3$ in C_6D_6) δ −69.2 (br s, 2F), −83.0 (t, 2F, $J = 12.1$ Hz), −86.4 (br s, 2F), −118.4 ppm (br s, 2F); MS (FAB) 469 (M + Na). Anal. Calcd for $C_4H_2F_8INaSO_5$: C, 10.35, H, 0.43. Found: C, 10.36, H, 0.26.

Unsaturated Carboxylic Acids. 4-Ethenylbenzoic acid, 4-phenyl-3-butenoic, and 4-pentenoic acid were obtained from Aldrich and used without further purification to prepare the sodium carboxylate salts. 4-(2-Propenyl)benzoic acid and (4-ethenylphenyl)acetic acid were prepared according to literature procedures.[23,24] 4-(1-Propenyl)benzoic acid was prepared by a procedure analogous to that used for 4-(2-propenyl)benzoic acid. Details of the procedures used for these preparations, as well as ^1H and ^{13}C NMR spectra of the compounds, are contained in the Supporting Information.

General Procedure for Preparation of Sodium Salts 2a−f of Unsaturated Carboxylic Acids. The following procedure is typical of those used to prepare the sodium salts of the unsaturated carboxylic acids (individual details, including ^1H NMR spectra of the salts, can be found in the Supporting Information):

Sodium *p*-Ethenylbenzoate (2a). *p*-Ethenylbenzoic acid (0.2348 g, 1.58 mmol) was dissolved in 5 mL of methanol in a 25 mL round-bottom flask equipped with a magnetic stir bar. Two drops of phenolphthalein solution (0.1% in ethanol) were added to the flask. NaOH solution (0.96 M in methanol) was added to the reaction mixture dropwise until the color of the mixture turned to light pink. Using a rotary evaporator, methanol was removed, giving a solid residue. The

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solid was washed with diethyl ether 3 times and dried under reduced pressure. The title compound was obtained in 85% yield:

^{1}H NMR (D_2O) δ 7.84 (d, 2H, $J = 8.1$ Hz), 7.55 (d, 2H, $J = 8.1$ Hz), 6.84 (dd, 1H, $J1 = 11.1$ Hz, $J2 = 17.4$ Hz), 5.93 (d, 1H, $J = 17.4$ Hz), 5.39 ppm (d, 1H, $J = 11.1$ Hz).

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Supporting Information Available: Details of synthesis, including NMR data, and tables and plots of kinetic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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