

values emphasises the similarity of $\text{Cl}\cdot$ and succinimidyl ($\text{S}_2\cdot$).

Addition competitions between benzene and *tert*-butylethylene with succinimidyl radical lead to the value ($k_{\text{C}_6\text{H}_6}/k_{\text{TBE}}$) = 2.0. Although values of 0.01–0.02 are reported for $\text{CH}_3\cdot$ and $\text{CF}_3\cdot$,⁸ there is precedent in $\cdot\text{OH}$ chemistry for relative rates of 1–4 for additions to substrates of this kind, reactions which occur with absolute rates of 10^8 – 10^9 $\text{L mol}^{-1} \text{ s}^{-1}$, encounter-controlled processes.⁹ Thus it seems reasonable to ascribe a similar absolute reaction rate to the $\text{S}_2\cdot$ succinimidyl radical additions to these substrates.

The substrate styrene is an especially interesting one since it has both alkene and arene moieties in the same molecule, and the vinyl group is generally considered to be unusually reactive for additions of radicals. Addition of 3,3-dimethylglutarimidyl radical occurs on the alkene 2.0 times as fast as to the arene portion of the molecule.

These results indicate that reactions of $\text{S}_2\cdot$, $\text{Cl}\cdot$, and $\cdot\text{OH}$ are similar and are relatively insensitive to structural features of the substrate. The transition states may be described in terms of a slightly perturbed substrate molecule with a nearby imidyl radical; by contrast, carbon radicals have stronger bonds to the substrates in both addition and abstraction reactions.^{8a}

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- (2) J. C. Day, M. J. Lindstrom, and P. S. Skell, *J. Am. Chem. Soc.*, **96**, 5616 (1974).
- (3) In the additions of NBS to olefins, substantial amounts of rearrangement product, β -bromopropionyl isocyanate, are generated. The troublesome side reaction can be minimized by using larger mole ratios of olefin/NBS and/or solvents in which NBS has poor solubility. The glutarimidyl system is free of this ring opening reaction.
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- (10) Undergraduate research scholars.

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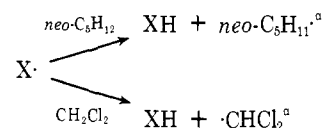
Excited-State Succinimidyl Radical in Thermal Chain Reactions

Sir:

The chemical properties of succinimidyl radicals remained a mystery until the simultaneous recognition in the laboratories of Professor J. G. Traynham¹ and ours² that the radical could be a chain carrier in the sense first suggested by Bloomfield,³ albeit incorrectly⁴ for the allylic bromination reaction.

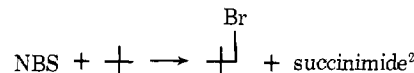
For substrates which react readily with bromine atoms, succinimidyl mediated brominations are carried out in the presence of bromine scavengers (ethylene or *tert*-butylethylene), employing a good solvent for NBS such as methylene chloride. In these circumstances bromination occurs with a selectivity which closely resembles $\text{Cl}\cdot$ mediated chlorinations.

Table I



Reagent ^b (no. of experiments; % yields)	$(k_{\text{neo-C}_5\text{H}_{11}}/k_{\text{CH}_2\text{Cl}_2})/H$
NBS-olefin (2; 4)	21.3 ± 2.0
NBS-Br ₂ (6; 14–96)	1.15 ± 0.16
NIS-I ₂ (4; 1–6) ^c	1.15 ± 0.12
NBP-olefin (2; 6–12)	12.1 ± 0.4
NBP-Br ₂ (5; 1–20)	0.51 ± 0.13
NIP-I ₂ (2; 5–11)	0.50 ± 0.02
NBDMG-olefin (2; 52)	3.9 ± 0.2
NBDMG-Br ₂ (1; 38)	1.0
Br ₂ ^d (1; 3)	0.1
Cl ₂ (2; 95)	>100

^a In all experiments *neo*-C₅H₁₁ \cdot is trapped to yield only neopentyl halide, while $\cdot\text{CHCl}_2$, in addition to being trapped with halogenating agent to yield CHXCl_2 , also adds to ethylene to yield, ultimately, 1,1-dichloro-3-halopropane. With low olefin and *N*-bromoimide concentration 1,1,2,2-tetrachloroethane from coupling of the dichloromethyl radical is observed. Relative rates in *N*-haloimide-olefin experiments were calculated using yields of neopentyl halide, halo-dichloromethane, halodichloropropane, and tetrachloroethane. ^b NXS = *N*-halosuccinimides; NXP = *N*-halophthalimides; NBDMG = *N*-bromo-3,3-dimethylglutarimide. ^c The NIS-allene system, in which I₂ is virtually eliminated, yields results similar to the NBS-olefin system. Although reliable quantitative results are not available in this case, unambiguously, the products from $\cdot\text{CHCl}_2$ were minor compared to neopentyl iodide. ^d Bromination is slow, 3% consumption of bromine after 4-h irradiation.



Glutarimidyl, 3,3-dimethylglutarimidyl, phthalimidyl, and several hydantoyl radicals also show hydrogen-abstraction properties.

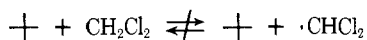
We make here a preliminary report that our results require the presence of two radicals in these systems, a ground state ($\text{S}_1\cdot$) and an excited state radical ($\text{S}_2\cdot$). This conclusion may have significance similar to that generated by the earlier suggestion that two carbene states were required to rationalize carbene chemistry.

Imidyl radicals can be generated as reaction intermediates in (1) the presence of bromine scavenger olefins, as indicated above, or (2) by the use of the *N*-haloimide and free halogen when using substrates which do not react readily with the bromine atom (neopentane, *tert*-butyl chloride, CH_2Cl_2 , as examples).⁵ The imidyl radicals generated by these two procedures show strikingly different reactivities. Results for competitive halogenations of neopentane and methylene chloride are shown in Table I.

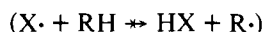
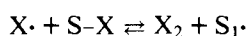
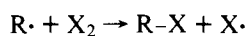
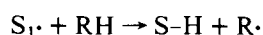
In all competitions, mole ratios of substrate (neopentane, CH_2Cl_2)/*N*-haloimide were 30 or more. The competitions with *N*-haloimide-olefin reagent were carried out using methylene chloride/neopentane mixtures (mole ratios between 8 and 300), methylene chloride functioning as both substrate and solvent; an *N*-haloimide/olefin ratio of 2.0 was generally used in order to keep addition product formation to a minimum. In competition experiments using *N*-haloimide-X₂ reagent, molar ratios of methylene chloride/neopentane between 2 and 16 were employed and *N*-haloimide/X₂ ratios of 0.5 to 100. All competition reactions were photoinitiated after degassing and were conducted at 15 °C. Bromoimide-Br₂ systems are efficiently initiated at wavelengths >400 nm; the bromoimide-olefin systems are initiated only with wavelengths between 280 and 350 nm. In bromination reactions irradiation times of

0.5–3.0 h were employed. Rates were considerably greater with the more soluble *N*-bromo-3,3-dimethylglutarimide than with the slightly soluble NBS and *N*-bromophthalimide. The same relative rates (for a given bromoimide) are obtained in homogeneous and heterogeneous reaction systems. ¹H NMR spectra of reaction mixtures and subsequent examination by GC indicated that the only products were the bromination products, the imides, small amounts of *N*-haloimide-olefin adduct, and the ring-opened product, β -bromopropionyl isocyanate, in the case of the NBS-olefin runs. Relative rates were calculated using product yields determined via GLC.

Exchange between product radicals and starting materials were demonstrated not to take place under these conditions by examining the recovered starting materials in an experiment using CD₂Cl₂ as solvent.



Identical relative rates are obtained with (bromoimides + Br₂) or (iodoimides + I₂) reagents (changes in concentration of X₂ had no effect on the relative rates), leaving no alternative but to ascribe the hydrogen abstracting steps to imidyl radicals; the imides are the only nitrogen-containing products. Under these conditions an imidyl radical (S₁·) is invoked. This imidyl radical shows equal reactivity toward the C–H bonds of CH₂Cl₂ and neopentane. Also, in the case of succinimidyl, *there is no opening of the ring to give product* BrCH₂CH₂C(=O)N=C=O.⁶ Since Br₂ and I₂ are much better radical trapping agents than the haloimides, three-step chain processes are required:

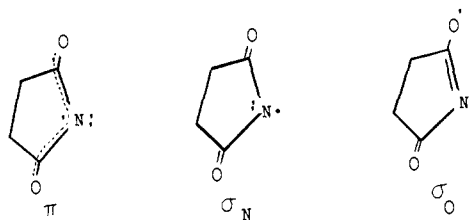


The third step, in which S₁· is regenerated is a near-thermo-neutral step.⁷

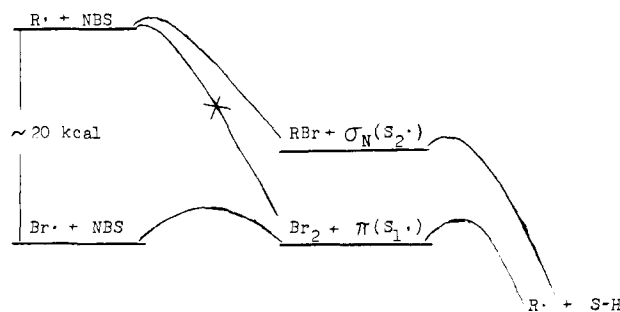
The reactions carried out in the presence of small amounts of bromine-scavenger olefins show a strikingly different selectivity, neopentane, despite its stronger C–H bonds, being considerably *more* reactive than CH₂Cl₂. Here too, changes in the olefin concentration had no effect on the relative rates. The nitrogen-containing product is the imide exclusively for the phthalimidyl and glutarimidyl system, succinimide and XCH₂CH₂C(=O)N=C=O for the succinimidyl systems, this latter ring-opened product accounting for 50–70% of the starting material. *It is impossible to explain the altered selectivity with a single hydrogen-abtracting imidyl radical since the rate competition between neopentane and methylene chloride does not involve the other materials added, the olefin or halogen;* the latter can only use some of the imidyl radicals in other reaction pathways, but *they cannot effect the competition* studied. For this reason we are forced to the conclusion that a *different* imidyl radical is involved (S₂·). This radical is generated in the exothermic (~20 kcal/mol) reaction of an alkyl radical with S–X. This radical is far less sensitive to the bond strength of its prey, and, *it undergoes the ring-opening reaction in the succinimidyl system.*



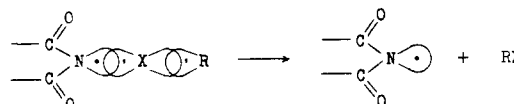
Some possible VB formulations for these radicals are the π , σ_N , σ_O representations; these represent orthogonal orbital systems which thereby cannot be considered as the canonical contributors to a hybrid structure. Koenig's INDO calculation⁸ on succinimidyl helps to identify S₁· with ground state π and S₂· with σ_N or σ_O excited states. Further, he recognized a



correlation of σ_O or σ_N with the open-chain isomeric radical, $\cdot\text{CH}_2\text{CH}_2\text{C(=O)C=N=O}$, but not with the π .⁸



While it is readily understandable that the thermo-neutral reaction of X· + S–X can lead only to ground state S₁·, it is not immediately obvious why the exothermic R· + S–X leads to S₂· rather than S₁·. A naive picture, with unpairing electrons in the σ_N orbital, may be a sufficient explanation but theoreticians may supply a better one.



Since there is no reason to expect unique energetics for the imidyl systems, analogous energetics may obtain in others, some obvious examples being π - and σ -aryl, -vinyl, -acyl and -acyloxy radicals, and even NO and NO₂ and the halogen atoms. If the energetics are suitable to reach a metastable excited state, there is no reason to exclude it as an intermediate. Well-established examples of excited states from thermal processes are singlet oxygen and the whole catalog of chemiluminescent systems.

We are searching actively for other examples of this type of behavior in various radical systems, examining a variety of substrates for their different responses to ground- and excited-state radicals, seeking examples of selective photoactivations, and attempting to obtain supporting spectroscopic data. The ring-opening behavior of S₂· succinimidyl is understood now and a report of this subject will be submitted shortly.

Acknowledgment. Financial support came from the Air Force Office of Scientific Research (2748C).

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- If the substrate reacts readily with a bromine atom (butane, 1-bromobutane, 2,3-dimethylbutane, as examples), the chain is carried by the bromine atoms to the complete exclusion of the imidyl radicals.
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Entropy Changes for the Protonation of Alkenes

Sir:

We wish to report experimentally determined entropy and enthalpy changes for proton transfers to olefins, which clarify inconsistencies in the literature, and give the first experimental values for the absolute entropies of tertiary alkyl ions.

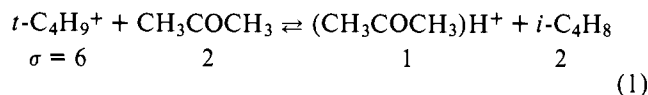
In recent studies of proton-transfer equilibria,¹ reaction enthalpies were derived from measured values for the free-energy change, ΔG° ,

$$-RT \ln K_{eq} = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (I)$$

making the assumption that the entropy change for the reaction can be predicted from changes in rotational symmetry numbers between products and reactants:

$$\Delta S^\circ (\text{proton transfer}) \approx \Delta S_{Rot} \approx R \ln (\sigma_{AH^+} \sigma_B / \sigma_{BH^+} \sigma_A) \quad (II)$$

However, a comparison of data from an ICR study^{1a} at 300 K with that from a high pressure mass spectrometric study^{1b} at 600 K reveals that there are reactant pairs for which "experimental" values of ΔS° show inconsistencies with eq II. In particular, the entropy change predicted for the equilibrium



was estimated to be +3.56 cal/(K mol) from eq II, assuming that the symmetry numbers are as shown above.^{1a,b} However, on this basis, the value for ΔG° measured at 600 K^{1b} should have been greater than the value determined at 300 K^{1a} by 1.1 kcal/mol (assuming, as usual, that ΔS° is approximately temperature independent). In fact the values determined^{1a,2} for ΔG° at 300 and at 600 K^{1b} differ by only 0.1 \pm 0.1 kcal/mol over this 300 K temperature range.

A determination of the entropy change associated with reaction 1 was carried out in the NBS pulsed ICR spectrometer.³ Equilibrium constants were determined in binary gas mixtures (pressure 10⁻⁶-10⁻⁵ Torr; observation time 0.2-0.3 s; temperature 300-400 K) in a pulsed ICR cell which can be ex-

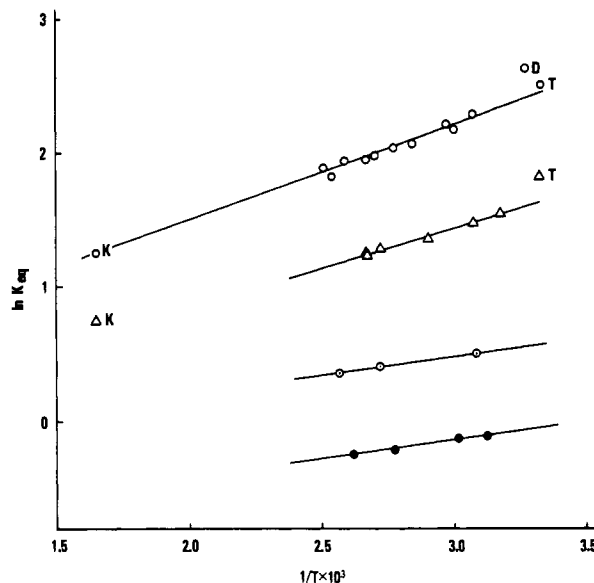
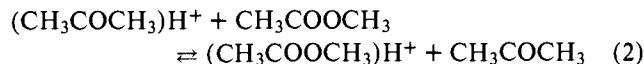


Figure 1. Plots of $\ln K_{eq}$ vs. $1/T$ for the equilibria: (1) (O); (2) (Δ); (3) (\odot); (4) (\bullet). Points labeled T are from ref 1a, K from ref 1b, and D from ref 2a.

ternally heated. Under these conditions, there was no evidence of ion loss due to the occurrence of competing reactions.^{2a} The resulting van't Hoff plot (Figure 1) indicates that, indeed, the entropy change for reaction 1 is 0.0 ± 0.3 cal/(K mol), rather than +3.56 cal/(K mol), assuming that ΔH_{Rn} is constant over the temperature range of the experiment.

In order to interpret this result it is important to note evidence that the entropy change associated with the protonation of acetone is 0. The value of ΔS° determined (Figure 1) for the process



is -0.45 ± 0.20 cal/(K mol). (This is in agreement with the value of -0.7 cal/(K mol) derived from values in the literature for K_{eq} at 300^{1a} and 600 K.^{1b}) As shown in Table I, this entropy change can be entirely attributed to the "intermolecular entropy change",⁴ $\Delta S_{Int} = R \ln Z_f/Z_r$, where Z_f and Z_r are, respectively, the ion-molecule collision rates in the forward and reverse directions.⁵ (This term approximates the configuration integral.) That is, for these reactants, ΔS_{Rot} (eq II) must be 0. The interpretation of this result is uncertain, but it implies either that the symmetry numbers for acetone and protonated acetone are the same (contrary to the assumption usually made), or that there is an additional contribution to ΔS° which cancels the contribution due to changes in external symmetry numbers. The same conclusion is indicated by the results presented in reference 1b, where an entropy change of $+0.16 \pm 0.4$ was determined for the equilibrium $(\text{CH}_3\text{COCH}_3)\text{H}^+ + \text{C}_2\text{H}_5\text{COOCH}_3 \rightleftharpoons (\text{C}_2\text{H}_5\text{COOCH}_3)\text{H}^+ + \text{CH}_3\text{COCH}_3$. For this equilibrium the entropy change

Table I. Entropy and Enthalpy Changes Determined for Proton-Transfer Reactions

Equilibrium	ΔH° , kcal/mol ^a	cal/(K mol)			
		Exptl $\Delta S^\circ =$	$\Delta S_{Rot}^b + \Delta S_{Int}^c + \Delta S_{Other}^d$		
$t\text{-C}_4\text{H}_9^+ + \text{CH}_3\text{COCH}_3 \rightleftharpoons (\text{CH}_3\text{COCH}_3)\text{H}^+ + i\text{-C}_4\text{H}_8$	-1.47 ± 0.20	0.0 ± 0.3	$+2.19^e$	$+1.14$	-3.3
$t\text{-C}_5\text{H}_{11}^+ + \text{CH}_3\text{COCH}_3 \rightleftharpoons (\text{CH}_3\text{COCH}_3)\text{H}^+ + (\text{CH}_3)_2\text{C}=\text{CHCH}_2$	-0.55 ± 0.05	-0.64 ± 0.10	0^e	$+0.77$	-1.4
$t\text{-C}_6\text{H}_{13}^+ + \text{CH}_3\text{COOCH}_3 \rightleftharpoons (\text{CH}_3\text{COOCH}_3)\text{H}^+ + (\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_3$	-0.50 ± 0.10	-1.7 ± 0.3	0^e	$+0.09$	-1.8
$(\text{CH}_3\text{COCH}_3)\text{H}^+ + \text{CH}_3\text{COOCH}_3 \rightleftharpoons (\text{CH}_3\text{COOCH}_3)\text{H}^+ + \text{CH}_3\text{COCH}_3$	-1.20 ± 0.06	-0.45 ± 0.02	0^e	-0.50	

^a 1 kcal/mol = 4.18 kJ. ^b Calculated from eq II. ^c $\Delta S_{Int} = R \ln Z_f/Z_r$; see discussion. The collision rates were calculated using the formulations of ref 5a-d. ^d Attributed to loss of internal rotation; see discussion. ^e See discussion and note 6.