Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 39. Bimolecular Self-Reactions of Some *N*-Alkylcarboxamidyl, *N*-Alkylsulfonamidyl, and *N*-Alkyl-*N*-(alkoxycarbonyl)aminyl Radicals. Intermolecular Hydrogen Atom Abstraction by *N*-Ethylpropionamidyl Radical[1]

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Abstract: Some *N*-alkylmethylsulfonamidyl radicals, $RNSO_2CH_3$, *N*-alkyl-*N*-(ethoxycarbonyl)aminyl radicals, $RNC(O)OC_2H_5$, and *N*-alkyl(trifluoromethyl)acetamidyl radicals, $RNC(O)CF_3$, have been generated by photolysis of the parent *N*-chloro amide or *N*-bromo amide in cyclopropane. From a comparison of their EPR parameters with those of *N*-alkylcarboxamidyl radicals, $RNC(O)R'$, it is concluded that all of these radicals have a π-electronic ground state. These radicals nearly all decay with clean second-order kinetics. Sterically unhindered amidyl radicals decay at rates equal or near to the diffusion-controlled limit, while sterically hindered amidyls, particularly those having R = *tert*-butyl, decay more slowly because there is a significant enthalpy barrier to their self-reaction. For the $(CH_3)_3CNSO_2CH_3$ radical, the kinetics are of mixed first (favored when the radical is generated from the *N*-chloro amide) and second (favored when the radical is generated from the *N*-bromo amide) order. The kinetics of the thermally initiated radical-chain halogenation of cyclohexane by *N*-chloro- and *N*-bromo-*N*-ethylpropionamide have been examined in benzene at 301 K. In the presence of added trichloroethylene, which supresses parallel halogenation carried by a halogen atom chain, the rate-controlling step for chain propagation is hydrogen atom abstraction from the cyclohexane by the $C_2H_5NC(O)C_2H_5$ radical. The results for chlorination and bromination are in good agreement and yield a rate constant for this abstraction of ca. 6.4×10^3 M^{-1} s^{-1}. The rate constant for reaction of $(CH_3)_3CNSO_2CH_3$ and cyclohexane is ≤ 0.04 M^{-1} s^{-1} at 293 K.

Studies on the chemistry of *N*-alkylcarboxamidyl radicals, $RNC(O)R'$, have concentrated almost exclusively on two topics.[4] First is the question of whether such radicals have a π- or σ-electronic ground state, both states having been suggested to participate in chemical reactions.[4b,c,5] This question has now been resolved in favor of the π state as a result of detailed examinations of the EPR spectra of a number of *N*-alkylcarboxamidyls over a wide range of temperatures.[6-9] Second is the use of *N*-alkylcarboxamidyl radicals as synthetic intermediates in reactions that generally involve free-radical chain processes, the radical either adding to a multiple bond or undergoing an inter- or intramolecular hydrogen atom abstraction.[4,5] Although there is now a very large body of qualitative information regarding the reactivities of *N*-alkylcarboxamidyl radicals, there has been only one serious attempt to obtain quantitative kinetic information.[10,11] This was by Tam, Yip, and Chow[10] who generated the $CH_3NC(O)CH_3$ radical by flash photolysis of *N*-nitroso-*N*-methylacetamide and studied the kinetics of its reactions with the parent nitrosoacetamide, with cyclohexane, and with *trans*-piperylene in benzene at room temperature. An unusual feature of their results was that even in the absence of reactive substrates, the radical still underwent a first-order decay.[13] Since the vast majority of small, sterically unhindered free radicals decay with second-order kinetics,[15,16] we decided to investigate the kinetics of the self-reactions of a number of the *N*-alkylcarboxamidyl radicals that we had already studied spectroscopically.[7] Using the technique of kinetic EPR spectroscopy,[16] we find that in cyclopropane all of the *N*-alkylcarboxamidyls that we investigated decayed with second-order kinetics, the rate constants for decay varying from the diffusion-controlled limit to ca. 0.1% of this limit.

We have also investigated some radicals that, though apparently closely related to the *N*-alkylcarboxamidyls, are reported to show somewhat different chemical properties—at least insofar as the products of certain free-radical chain reactions are concerned. Most notable in this respect are the *N*-alkylsulfonamidyl radicals,[17-20] $RNSO_2R'$, the *N*-alkyl-*N*-(alkoxycarbonyl)aminyl radicals,[21-26] $RNC(O)OR'$, and the *N*-alkyl(trifluoromethyl)acet-

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amidyl radicals,[21,22,24,25] $R\dot{N}C(O)CF_3$. Although EPR spectral parameters have been reported for a number of sulfonamidyl radicals in solution, these have generally been measured at only a single temperature.[9,27-32] Parameters for the $H\dot{N}C(O)CF_3$ radical in a single crystal have also been reported.[33] We have therefore undertaken both a limited, variable temperature EPR spectroscopic study of some $R\dot{N}SO_2CH_3$, $R\dot{N}C(O)OC_2H_5$, and $R\dot{N}C(O)CF_3$ radicals and a kinetic study of the bimolecular self-reactions of the $R\dot{N}SO_2CH_3$ and $R\dot{N}C(O)OC_2H_5$ radicals.

In addition, we have investigated the kinetics of the free-radical chain halogenation of cyclohexane by *N*-chloro- and *N*-bromo-*N*-ethylpropionamide at 301 K. The absolute rate constant for hydrogen abstraction from cyclohexane by the $C_2H_5\dot{N}C(O)C_2H_5$ radical was found to be in reasonable agreement with the value obtained previously by Tam et al.[10] for the analogous reaction with $CH_3\dot{N}C(O)CH_3$.

Experimental Section

Materials. The *N*-chloro-*N*-alkylcarboxamides were prepared from the parent amides by reaction with chlorine in aqueous sodium bicarbonate as described by Orton and Bradfield.[34] The completeness of reaction (i.e., the purity of the chloroamide) was checked by ^1H NMR, monitoring either the loss of the signal due to N*H* or the downfield shift of the signal due to NC*H*. The chloroamide was extracted with methylene chloride, washed with water, and dried over anhydrous Na_2SO_4, the solvent was removed under vacuum, and final purification was by bulb-to-bulb distillation. The *N*-bromo-*N*-alkylcarboxamides were pepared by various literature methods.[35-37] The purest product and the one easiest to work up was obtained by direct treatment of the amide with bromine and aqueous sodium bicarbonate at 0–5 °C.[37] The completeness of reaction was again checked by ^1H NMR, and workup was the same as for the chloro amides. The methylsulfonamides,[19] ethylcarbamates,[38] and trifluoroacetamides,[39] were prepared by literature methods. They also were converted to the corresponding *N*-halo compounds by using Cl_2 or Br_2 and sodium bicarbonate and were then purified by bulb-to-bulb distillation or recrystallization. *tert*-Butyl hyponitrite was prepared by the method of Kiefer and Traylor.[40] All other materials were of the highest purity commercially available.

Radical-Decay Kinetics. The general experimental procedures of the kinetic EPR technique have been described previously.[16] The various amidyl radicals were generated directly in the cavity of a Varian E-4 EPR spectrometer by UV photolysis of the parent *N*-chloro amide[6-9,41]

Table I. EPR Spectral Parameters for Some *N*-Alkylamidyl Radicals in Cyclopropane[a]

		$R\dot{N}SO_2CH_3$			$RNC(O)OC_2H_5$			$RNCOCF_3$				$RNCOC_2H_5$[b]		
R	T, K	g	a^N	$a^{H\beta}$(R)	g	a^N	$a^{H\beta}$(R)	g	a^N	$a^{H\beta}$(R)	a^F	g	a^N	$a^{H\beta}$(R)
CH_3	198–293	2.0043_6[c]	13.2[c]	29.7[c,d]								2.0055	14.9	29.5[d]
CH_3CH_2	203	2.0043_5[e]	13.0_5[e]	38.6_5[e,f]								2.0052	14.6	37.4[f]
	248	2.0043_6[e]	13.0_6[e]	36.4_9[e,f]								2.0052	14.6	35.7[f]
	293	2.0043_6[e]	13.0_6[e]	35.1_3[e,f]								[g]	[g]	[g]
$(CH_3)_3CCH_2$	158				2.0048	15.01	43.33[f]					2.0053	14.9	40.4[f]
	222				2.0050	15.07	41.47[f]					2.0053	14.9	38.9[f]
	273				[g]	15.0	40.0[f]					2.0053	14.8	37.9[f]
$(CH_3)_2CH$	166	2.003_9[h]	13.0_4[h]	5.9_4[h]	2.0046	14.71	32.11[i]	[g]	[g]	[g]	[g]	2.0050	14.5	26.6[i]
	203	2.0041_2[h]	13.0_6[h]	6.4_5[h,i,j]	[g]	[g]	[g]	2.0057	13.95	21.94[i]	2.1[k]	[g]	[g]	[g]
	213	2.0041_2[h]	13.0_6[h]	6.8_4[h]	[g]	[g]	28.95[i]	[g]	[g]	[g]	[g]	2.0050	14.5	25.0[i]
	233	2.0041_3[h]	13.0_7[h]	7.4_4[h]	2.0048	14.76	28.95[i]	[g]	[g]	[g]	[g]	2.0050	14.5	24.5[i]
	248	2.0041_3[h]	13.0_7[h]	8.0_8[h]	[g]	[g]	[g]	[g]	[g]	[g]	[g]	[g]	[g]	[g]
	268	2.0041_3[h]	13.0_8[h]	8.7_9[h]	2.0047	14.69	28.18[i]	[g]	[g]	[g]	[g]	2.0050	14.5	24.0[i]
	293	2.0041_4[h]	13.0_8[h]	9.6_1[h]	[g]	[g]	[g]	[g]	[g]	[g]	[g]	[g]	[g]	[g]
$(CH_3)_3C$	158–293[l]	2.0043_2[m]	13.3[m,n]	[o]	2.0045	15.7[p]	[q]	2.0051	15.1[r]		3.75[k]	2.0045	15.6	[s]

[a] Hyperfine splittings are given in gauss. [b] Data are from ref 7. [c] Reference 9 gives $g = 2.0041$, $a^N = 13.4$ G, $a^{H\beta} = 29.7$ G at 303 K. [d] 3 H. [e] Reference 9 gives $g = 2.0041$, $a^N = 13.2$ G, $a^{H\beta} = 35.7$ G at 303 K. [f] 2 H. [g] Not measured. [h] Reference 9 gives $g = 2.0041$, $a^N = 13.09$ G, $a^{H\beta} = 8.70$ G, $a^{H\gamma}(6\text{ H}) = 0.92$ G at 273 K. [i] 1 H. [j] $a^{H\gamma}(6\text{ H}) = 0.92$ G. [k] 3 F. [l] Temperature range not covered for all radicals. [m] Reference 27 gives $g = 2.0044$, $a^N = 12.9$ G, $a^H(9\text{ H}) = 0.68$ G at 223 K and a spectrum. [n] 13.23 G at 203 K, 13.39 G at 248 K, 13.47 G at 293 K. [o] Additional H hfsc observable from $(CH_3)_3C$ and from SO_2CH_3 groups, see ref 27. [p] 15.5 G at 158 K, 15.7 G at 192 K. [q] $a^H(9\text{ H}) = 0.55$ G. [r] At 212 K. [s] $a^H(9\text{ H}) = 0.56$ G for $(CH_3)_3C\dot{N}COCH_3$.

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or of *N*-bromo amide in deoxygenated cyclopropane as solvent.

Halogenation Kinetics. The radical chain halogenation of cyclohexane by $C_2H_5N(Cl)C(O)C_2H_5$ or by $C_2H_5N(Br)C(O)C_2H_5$ was initiated by the thermal decomposition of *tert*-butyl hyponitrite with benzene as the solvent. Most samples also contained 5–10 mol %, on the basis of the initial chloro amide or bromo amide concentration, of trichloroethylene. This was added to suppress any concurrent halogen atom chain reaction (see Results). Samples were made up in standard 5-mm o.d. NMR tubes and, after degassing by the freeze–thaw method, were sealed under vacuum. All reactions were run at 301 K in the probe of a Varian EM 360 A NMR spectrometer. The progress of the reaction was monitored by following the decrease of the CH_2 signal of the *N*-ethyl group of the halo amide (δ 3.71, q, J = 7 Hz for chloro amide; δ 3.58, q, J = 7 Hz for bromo amide) and the increase in this signal for the amide (δ 2.83, d of q, J = 7 Hz).

Results

EPR Spectra. The EPR spectral parameters for all the *N*-alkylcarboxamidyl radicals described in this paper have been reported previously.[7] Parameters for the $R\dot{N}SO_2CH_3$, $R\dot{N}C(O)OC_2H_5$, and $R\dot{N}C(O)CF_3$ radicals are given in Table I together with those previously reported[6,7] for the corresponding $R\dot{N}C(O)C_2H_5$ radicals measured under similar conditions.[42] As is noted in this table, the parameters for the four methylsulfonamidyl radicals examined in this work have been previously reported at one temperature.[9,27] The other radicals were unknown. All the $R\dot{N}C(O)CF_3$ radicals gave a strong EPR signal initially, but these signals disappeared after quite a brief period of UV irradiation, even at low temperatures in cyclopropane. It was therefore difficult (and occasionally impossible, e.g., R = neopentyl) to measure the EPR spectral parameters for these radicals, and we were quite unable to obtain reliable decay kinetics.

Radical-Decay Kinetics. With one exception, all the amidyl radicals studied in this work decayed with "clean" second-order kinetics in cyclopropane as solvent, and the radical concentrations under steady illumination were proportional to the square root of the incident light intensity. The rate constants for decay, $2k_t$,

$$R\dot{N}Z + R\dot{N}Z \xrightarrow{2k_t} \text{products}$$

were not affected by the initial radical concentration (which was changed by varying the initial light intensity) or by generating the radical from the *N*-bromo amide rather than from the *N*-chloro amide. These "normal" radicals and their measured decay rate constants are listed in Table II together with the Arrhenius parameters in those cases in which measurements were made over a range of temperatures. The reproducibility of the individual rate constants was generally better than ca. ±30%. However, we would not claim that their overall reliability was any better than a factor of 2 because of the usual uncertainties involved in determining absolute radical concentrations. As was mentioned above, it was not possible to measure the rate constant for decay of any $R\dot{N}C(O)CF_3$ radical. However, experiments at different light intensities did suggest that decay probably followed second-order kinetics.

The *N*-*tert*-butylsulfonamidyl radical showed exceptional behavior in that its decay followed mixed first- and second-order kinetics. What was more surprising, the first-order decay process was dominant when the radical was generated from the *N*-chloro sulfonamide, while the second-order decay process was dominant when the *N*-bromo sulfonamide was used as the radical source. For most individual runs, the decay of the radical derived from the chlorosulfonamide followed reasonably clean first-order kinetics from which a first-order rate constant could be readily obtained. However, these rate constants increased slightly with increasing radical concentration, particularly at low temperatures (see Table III).[43] This suggests that there is some incursion of the second-order decay process at the higher concentrations. In contrast, for most individual runs, the decay of the radical derived from

Table II. Rate Constants and Arrhenius Parameters for the Bimolecular Self-Reactions of Some $R\dot{N}C(O)R'$, $R\dot{N}SO_2CH_3$, and $R\dot{N}C(O)OC_2H_5$ Radicals in Cyclopropane[a]

radical	T, K	$10^{-7}2k_t$, M^{-1} s^{-1}	log A, M^{-1} s^{-1}	E_a, kcal/mol
$CH_3\dot{N}C(O)C(CH_3)_3$	208	82		
$C_2H_5\dot{N}C(O)C_2H_5$	208	410		
$(CH_3)_3CCH_2\dot{N}C(O)CH_3$	208	85		
$(CH_3)_2CH\dot{N}C(O)CH_3$	208	460		
$(CH_3)_2CH\dot{N}C(O)C_2H_5$	208	98		
$(CH_3)_3C\dot{N}C(O)CH_3$	208	0.11		
$(CH_3)_3C\dot{N}C(O)C_2H_5$	208	0.04		
$(CH_3)_3C\dot{N}C(O)C(CH_3)_3$	206	0.023	11.0	5.1
	210	0.036		
	228	0.10		
	245	0.22		
	267	0.56		
	281	0.80		
$CH_3\dot{N}SO_2CH_3$	213	160	10.6	1.4
	213	200		
	243	250		
	253	240		
	253	330		
	293	430		
	293	460		
$C_2H_5\dot{N}SO_2CH_3$	213	93	9.9	0.9
	213	91		
	253	140		
	293	170		
$(CH_3)_2CH\dot{N}SO_2CH_3$	213	1.8	10.5	3.1
	233	3.3		
	253	5.0		
	253	5.6		
	263	10.2		
	293	12.4		
$(CH_3)_3C\dot{N}SO_2CH_3$		*b*	ca. 8.8[c]	ca. 6.0[c]
$(CH_3)_2CH\dot{N}C(O)OC_2H_5$	210	130		
$(CH_3)_3C\dot{N}C(O)OC_2H_5$	210	0.26	10.8	4.1
	236	1.36		
	262	2.8		
	283	4.0		

[a] Rate constants are averages of two or more individual experiments usually involving different initial radical concentrations and, in some cases, radical generation from both the chloro amide and the bromo amide. Deviations from the mean were generally <30%. [b] See text and Table III. [c] Approximate Arrhenius parameters based on the second-order decay of the radical generated from the bromosulfonamide.

Table III. Rate Constants for the Decay of $(CH_3)_3C\dot{N}SO_2CH_3$ Radicals Derived from Parent *N*-Chloro- and *N*-Bromosulfonamides in Cyclopropane

T, K	$10^5(CH_3)_3C\dot{N}SO_2CH_3$, M[a]	k, s^{-1} [b] (chloro amide)	$10^{-3}k$, M^{-1} s^{-1} [b] (bromo amide)
213	0.5	0.065	
	3.0	0.08	
	30	0.18	
233	0.5		12
	3.0		6.9
	30	0.26	2.1
253	0.5	0.27	17
	5	0.32	3.8
	30	0.43	2.5
273	0.5	0.54	
	3	0.57	9.1
	30		4.1
293	0.5	1.3	24
	5	1.5	19
	30	1.3	9.9

[a] Although radical concentrations were measured accurately, only approximate initial concentrations are given here in order to simplify the table. [b] Most rate constants are averages of two or more separate measurements.

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Table IV. Rates of Reaction of *N*-Halo-*N*-ethylpropionamides with Cyclohexane in Benzene at 301 K Initiated with TBHN

			$C_2H_5N(Cl)C(O)C_2H_5$			$C_2H_5N(Br)C(O)C_2H_5$		
[amide], M	$[C_6H_{12}]$, M	10^2[TBHN], M	$10^4\rho$, M s^{-1}	$\frac{\rho}{[C_6H_{12}](R_i)^{1/2}}$	$\frac{\rho}{[\text{amide}](R_i)^{1/2}}$	$10^4\rho$, M s^{-1}	$\frac{\rho}{[C_6H_{12}](R_i)^{1/2}}$	$\frac{\rho}{[\text{amide}](R_i)^{1/2}}$
0.7	3.9	4.4	1.6	0.12	0.67	0.9	0.07	0.39
1.4	3.9	4.4	1.3	0.10	0.27	1.4	0.10	0.38
2.3	3.9	4.4	4.0	0.29	0.49	3.3	0.24	0.41
1.4	2.0	4.4	3.7	0.27	0.39			
1.4	7.3	4.4	2.1	0.08	0.42	2.8	0.11	0.57
1.4	3.9	1.7	2.2	0.26	0.72	0.8	0.09	0.25
1.4	3.9	2.2	2.0	0.21	0.59	1.0	0.10	0.28
1.4	3.9	6.3	2.3	0.14	0.39	2.4	0.15	0.42
1.4	3.9	8.8	5.8	0.30	0.84			
1.4	3.9	18	⩾50	⩾1.8	⩾5.0	6.0	0.22	0.61
1.4	0	8.8	3.5	∞	0.50	1.7	∞	0.24

the *N*-bromo sulfonamide followed reasonably clean second-order kinetics. However, the calculated second-order rate constants show a quite pronounced decrease with increasing concentration of radical (see Table III),[43] which suggests that there is a significant contribution to decay from the first-order process at the lower concentrations.

The nature of the first-order decay process and the reason that it should be so much more important when the radical is generated from the *N*-chloro sulfonamide are unknown. The Arrhenius parameters derived from the first-order decays at low initial radical concentrations and at the higher temperatures[43] (so as to reduce the importance of the second-order process) are $A \approx 10^{4.7}$ s^{-1}, $E_a \approx 6.1$ kcal/mol. The low value of the preexponential factor does not seem appropriate for a true unimolecular reaction.

The Arrhenius plots of the second-order rate constants calculated at initial $(CH_3)_3CNSO_2CH_3$ concentrations of ca. 3×10^{-5} and ca. 3×10^{-4} M, for which the contribution from first-order decay should be negligible, are curved unless the data at 233 K are ignored. If this is done, the derived Arrhenius parameters[43] are $A \approx 10^{8.8}$ M^{-1} s^{-1}, $E_a \approx 6.0$ kcal/mol. It is perhaps worth pointing out that neither $(CH_3)_3CNC(O)C(CH_3)_3$ nor $(CH_3)_3CNC(O)OC_2H_5$ show any sign of first-order decay, though they were generated from their *N*-chloro parents. However, the bimolecular decay of both of these radicals is much faster than that of $(CH_3)_3CNSO_2CH_3$.

Free-Radical Chain Halogenation of Cyclohexane. The reaction of *N*-chloro- and *N*-bromo-*N*-ethylpropionamide with cyclohexane was studied in benzene at 301 K in the probe of an NMR spectrometer. These two haloamides were chosen because they yield a representative unhindered amidyl radical, are relatively soluble and form soluble products, and the progress of the reaction could be easily monitored (see Experimental Section). The reactions were initiated by the thermal decomposition of *tert*-butyl hyponitrite (TBHN).

$$Me_3CONNOCMe_3 \xrightarrow{k_i} 2Me_3CO\cdot + N_2$$

The rate constant, k_i, for this reaction can be calculated to be 2.15×10^{-6} s^{-1} at 301 K.[40] The efficiency (e) of chain initiation was taken to be 66%, the value found in chlorobenzene at 303 K.[44] The rate of chain initiation is therefore given by

$$R_i = 2ek_i[\text{TBHN}] = (2.84 \times 10^{-6})[\text{TBHN}] \quad (I)$$

Reactions were relatively rapid, but they were always preceded by an induction period (see Figure 1) of variable length that we tentatively attribute to traces of O_2 and other potential inhibitors of free-radical chain processes. Reaction did not occur in the absence of TBHN. The reaction rate, ρ, was calculated from the region in which the halo amide concentration was decreasing most rapidly.

(43) By no means have all of the kinetic data obtained with this radical been presented in Table III.

(44) Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 6478–6485.

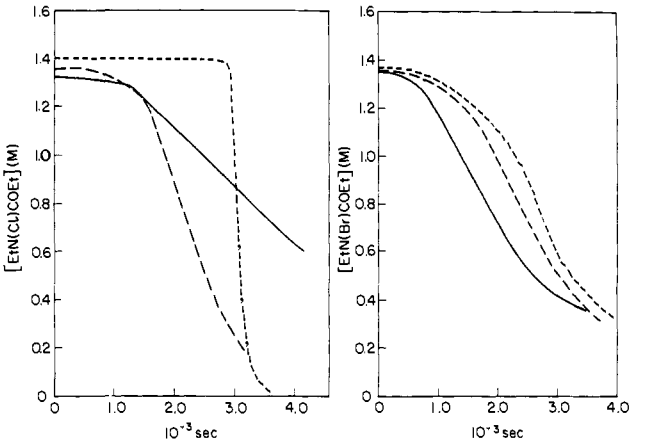

Figure 1. *N*-Halo-*N*-ethylpropionamide concentration as a function of time at different C_2HCl_3 concentrations: (—) 0.14 M C_2HCl_3, (– – –) 0.07 M C_2HCl_3, (- - -) 0.03 M C_2HCl_3 for chloro amide, 0 C_2HCl_3 for bromo amide. Cyclohexane = 3.9 M, reactions initiated with 0.18 M TBHN in benzene at 28 °C.

For such chain reactions, the overall process can be represented as follows:

Initiation

production of radicals; rate = R_i

Propagation

$$C_6H_{11}\cdot + C_2H_5N(X)C(O)C_2H_5 \rightarrow C_6H_{11}X + C_2H_5\dot{N}C(O)C_2H_5 \quad (1)$$

$$C_2H_5\dot{N}C(O)C_2H_5 + C_6H_{12} \rightarrow C_2H_5NHC(O)C_2H_5 + C_6H_{11}\cdot \quad (2)$$

Termination

$$C_6H_{11}\cdot + C_6H_{11}\cdot \rightarrow \text{nonradical products} \quad (3)$$

$$C_6H_{11}\cdot + C_2H_5\dot{N}C(O)C_2H_5 \rightarrow \text{nonradical products} \quad (4)$$

$$C_2H_5\dot{N}C(O)C_2H_5 + C_2H_5\dot{N}C(O)C_2H_5 \rightarrow \text{nonradical products} \quad (5)$$

If step 1 of this chain is rate controlling, the overall rate of reaction will be given by

$$\rho = \frac{k_1[C_2H_5N(X)C(O)C_2H_5](R_i)^{1/2}}{(2k_3)^{1/2}} \quad (II)$$

That is, the rate will be independent of the cyclohexane concentration but will depend on both the nature (i.e., X = Cl or Br) and concentration of the halo amide. If step 2 is rate controlling, then

$$\rho = \frac{k_2[C_6H_{12}](R_i)^{1/2}}{(2k_5)^{1/2}} \quad (III)$$

Table V. Effect of Added Trichloroethylene on the Rates of Reaction of *N*-Halo-*N*-ethylpropionamides with Cyclohexane in Benzene at 301 K Initiated with TBHN

	$10^4\rho$(M s^{-1}) for $[C_2H_5N(Cl)C(O)C_2H_5]$ = 1.3 M		$10^4\rho$(M s^{-1}) for $[C_2H_5N(Br)C(O)C_2H_5]$ = 1.3 M	
$[C_2HCl_3]$, M	$[C_6H_{12}]$ = 0; [TBHN] = 0.09 M	$[C_6H_{12}]$ = 3.9 M; [TBHN] = 0.18 M	$[C_6H_{12}]$ = 0; [TBHN] = 0.09 M	$[C_6H_{12}]$ = 3.9 M; [TBHN] = 0.18 M
0	3.5	>50	1.7	6.0
0.03		>26		
0.07	0.6	7.5	1.1	4.6
0.11		2.9		
0.14	0.2	2.5		4.4

and the rate will be independent of the halo amide but will depend on the cyclohexane concentration.

Some of our initial results are summarized in Table IV. It is obvious that the experimental rates do not fit with either eq II or eq III. It is clear, moreover, that the halo amide is consumed at an appreciable rate even in the absence of cyclohexane (see last line in Table IV). In chain reactions involving organic halogenating agents, kinetic problems of this general sort are not entirely unexpected.[45] One reason for the difficulty in obtaining reliable relative or absolute rate constants in such systems is the partial (or complete) incursion of a parallel halogenation in which the halogen atom is the chain carrier,[45] i.e., the parallel operation of a Goldfinger type of mechanism.[46] This problem is generally circumvented, more or less successfully, by the addition of reagents that either preferentially trap the atom X· without regenerating HX or trap the HX or X_2 (which are essential molecular intermediates in a Goldfinger type of process). Some of the more popular atom traps are olefins such as trichloroethylene[47-49] and *tert*-butylethylene,[50,51] and some of the more popular acid traps are bases such as 2,4,6-trimethylpyridine,[51,52] powdered potassium carbonate,[53] and certain other compounds such as ethylene oxide.[53] We found that under our free-radical conditions, the *N*-halo amides reacted quite rapidly with trimethylpyridine and ethylene oxide at the concentrations of these materials that would be necessary to suppress the halogen atom chain. Furthermore, these compounds yielded insoluble material that interfered with the NMR monitoring of the reaction. Trichloroethylene did not appear to suffer from these disadvantages. It was a powerful inhibitor of both the haloamide self-reaction and of its reaction with cyclohexane (see Figure 1 and Table V). As little as 5 mol % $[C_2HCl_3]$ based on the initial bromo amide concentration and 10 mol % based on the initial chloro amide concentration served to reduce the rate to an essentially constant value. These quantities of trichloroethylene were therefore employed in further work.

A second possible reason for the difficulty in extracting meaningful kinetic data from these reactions, and also perhaps for the occurrence of reaction in the absence of cyclohexane, would be the involvement of the benzene solvent in the chain process.[54-56]

Table VI. Rates of Reaction of *N*-Chloro-*N*-ethylpropionamide with Cyclohexane in Benzene Containing Trichloroethylene (10 mol % Based on Chloro Amide) at 301 K Initiated with TBHN

[amide], M	$[C_6H_{12}]$, M	10^2[TBHN], M	$10^4\rho$, M s^{-1}	$10^4\rho_{corr}$, M s^{-1}	$\frac{\rho_{corr}}{[C_6H_{12}](R_i)^{1/2}}$
1.3	0	8.8	0.2	0	
0.5	3.9	8.8	1.6	1.5	0.077
1.3	3.9	8.8	1.9	1.7	0.087
2.1	3.9	8.8	1.9	1.6	0.082
1.3	2.0	8.8	0.9	0.7	0.070
1.3	6.2	8.8	3.2	3.0	0.097
1.3	3.9	2.2	0.8	0.7	0.072
1.3	3.9	15	2.4	2.1	0.083
1.3	3.9	18	2.5	2.2	0.079

Table VII. Rates of Reactions of *N*-Bromo-*N*-ethylpropionamide with Cyclohexane in Benzene Containing Trichloroethylene (5 mol % Based on Bromo Amide) at 301 K Initiated with TBHN

[amide], M	$[C_6H_{12}]$, M	10^2[TBHN], M	$10^4\rho$, M s^{-1}	$10^4\rho_{corr}$, M s^{-1}	$\frac{\rho_{corr}}{[C_6H_{12}](R_i)^{2/2}}$
1.3	0	8.8	1.1		
0.7	3.9	8.8	2.1	1.5	0.077
1.3	3.9	8.8	2.9	1.8	0.092
2.4	3.9	8.8	3.6	1.6	0.082
1.3	2.0	8.8	1.8	0.7	0.070
1.3	6.2	8.8	3.6	2.5	0.081
1.3	3.9	2.2	1.1	0.8	0.082
1.3	3.9	18	4.6	3.0	0.11

However, a GC/MS analysis of the products from a typical reaction (1.4 M *N*-chloro-*N*-ethylpropionamide, 3.9 M cyclohexane in benzene containing 10 mol % C_2HCl_3 initiated with 4.4×10^{-2} M TBHN) carried to 80% completion showed reactants and products at the following approximate concentrations: chloro amide 0.3 M, amide 1.1 M, cyclohexane 2.8 M, and chlorocyclohexane 1.1 M. Compounds that might have been formed by the initial addition of the amidyl radical to the benzene were present in concentrations <0.02 M.

Kinetic data for the C_2HCl_3-inhibited reaction of *N*-chloro- and *N*-bromo-*N*-ethylpropionamide with cyclohexane are given in Tables VI and VII, respectively. Under the same conditions, the rates with the bromo amide are ca. 50% larger than the rates with the chloro amide. *However*, the C_2HCl_3-inhibited bromo amide self-reaction is much faster than the C_2HCl_3-inhibited chloroamide self-reaction (see top line in Tables V and VI). This led us to calculate "corrected" rates (ρ_{corr}) by subtracting from the experimental rate (ρ) an appropriate contribution, $\rho_{halo\ amide}$, for the haloamide self-reaction. Since $\rho_{halo\ amide}$ was measured at only one halo amide and one TBHN concentration, it was estimated for other conditions according to the assumed rate law: $\rho_{halo\ amide} = C[halo\ amide](R_i)^{1/2}$. The success of this procedure, and it is to be hoped its appropriateness, is attested to if the corrected rates are treated according to eq III, i.e., if ρ_{corr} is divided by the cyclohexane concentration and by the square root of the rate of chain initiation. As the final columns in Tables VI and VII indicate, this yields a quantity that is essentially invariant and, moreover, one that is virtually identical for the *N*-chloro amide (mean = 0.081 ± 0.016 $M^{-0.5}$ $s^{-0.5}$) and the *N*-bromo amide (mean = 0.085 ± 0.023 $M^{-0.5}$ $s^{-0.5}$) where the error limits correspond to two standard deviations (i.e., 95% confidence limits).

The *N*-*tert*-butylmethylsulfonamidyl radical was found to be very much less reactive toward cyclohexane. For example, with the *N*-bromo sulfonamide in neat cyclohexane at 293 K and with initial radical concentrations in the range $0.1-1.0 \times 10^{-5}$ M, the EPR-monitored decay followed fairly clean first-order kinetics with a mean rate constant of 0.4 ± 0.2 s^{-1}. This puts an upper limit of ca. 0.04 M^{-1} s^{-1} for the rate constant for H-atom abstraction from cyclohexane by this radical.

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Discussion

Electronic Ground State of Amidyl Radicals. We have shown previously by detailed analysis of the magnitude and temperature dependence of the EPR parameters of *N*-alkylcarboxamidyl radicals that these species have a π-electronic ground state.[6,7] Danen and Gellert[9] have used our arguments and their results with the *N*-isopropylphenylsulfonamidyl radical to support a π-electronic ground state for sulfonamidyl radicals, and such a ground state is also indicated by other EPR spectroscopic data.[9,27,30,31] Our own, more extensive study of the temperature dependence of the EPR parameters of sulfonamidyl radicals provides further support for a π-electronic ground state (cf. data for $R\dot{N}SO_2CH_3$ and $R\dot{N}C(O)C_2H_5$ in Table I). The most notable spectroscopic difference between sulfonamidyl and carboxamidyl radicals lies in the magnitude of the hyperfine splitting by the NC*H* protons (i.e., $a^{H_\beta}(R)$) for R = isopropyl.[9] The much smaller value of $a^{H_\beta}(R)$ for $(CH_3)_2CH\dot{N}SO_2CH_3$ compared with $(CH_3)_2CH\dot{N}C(O)C_2H_5$ implies that the tertiary C–H bond of the isopropyl group lies more nearly in the nodal plane of the semioccupied N 2pz orbital in the former radical than in the latter. This can be attributed to there being more steric hindrance between the two methyl groups for the isopropyl moiety and the two oxygen atoms of the SO_2 group than between the two methyl groups and the single oxygen atom of the CO group. In addition, the $(CH_3)_2CH\dot{N}SO_2CH_3$ radical probably has a single potential energy minimum in which the tertiary C–H bond lies exactly in the N $2p_z$ nodal plane. In contrast, the $(CH_3)_2CH\dot{N}C(O)C_2H_5$ radical probably has a double minimum in its potential energy surface, with the tertiary C–H bond lying slightly above or below the N $2p_z$ nodal plane in order to minimize its steric interaction with the carbonyl's oxygen atom. Other differences between the EPR parameters of sulfonamidyl and carboxamidyl radicals have been noted and discussed in the literature.[9,27,32b]

The EPR parameters including, in particular, the magnitude and temperature dependence of $a^{H_\beta}(R)$ are very similar for the $R\dot{N}C(O)OC_2H_5$ radicals and the comparable $R\dot{N}C(O)C_2H_5$ radicals (see Table I), which indicates that the former radicals also have a π-electronic ground state.

The EPR data for $R\dot{N}COCF_3$ radicals, though not extensive, are also compatible with a π-electronic ground state. For the $(CH_3)_2CH\dot{N}C(O)CF_3$ radical, the value of a^{H_β}, which is independent of temperature within experimental error, is smaller while the *g* values for this radical and for the $(CH_3)_3C\dot{N}C(O)CF_3$ radical are larger than for the comparable $R\dot{N}C(O)C_2H_5$ radicals. Although an electronic effect cannot be ruled out, it seems more probable that these changes reflect the substantial steric demands of the CF_3 group, which will induce a twisting of the $CF_3C(O)$ group out of the RNC plane. We have previously invoked such twisting to explain the reduced a^{H_β} values and increased *g* factors for $R\dot{N}C(O)R'$ radicals having R′ = *t*-Bu compared with those having R′ = Me, Et, etc.[7] For comparison with the data in Table I, it is worth noting that the $(CH_3)_2CH\dot{N}COC(CH_3)_3$ radical has[7] $g = 2.0053_5$ and $a^{H_\beta} = 21.5$ G at 213 K and the $(CH_3)_3C\dot{N}COC(CH_3)_3$ radical has[7] $g = 2.0051$. We suggest that at least some of the reported chemical differences between $R\dot{N}C(O)R'$ radicals and $R\dot{N}SO_2R'$, $R\dot{N}C(O)OR'$, and $R\dot{N}C(O)CF_3$ radicals (see Introduction) should be attributed to steric factors and not to differences in the electronic effects of the various acyl moieties.

Amidyl Radical Bimolecular Self-Reactions. All the amidyl radicals studied in this work decayed with second-order kinetics in cyclopropane (see Table II). This includes even the relatively persistent $(CH_3)_3C\dot{N}SO_2CH_3$ radical, provided it was generated from bromo amide (see Table III). The products of decay are presumably those of dimerization and, for appropriate structures, disproportionation. A GC/MS examination of the products of photolysis of $C_2H_5N(Cl)C(O)C_2H_5$ in cyclopropane indicated that >25 compounds had been formed including mono-, di-, and trichlorinated amides and 1,2- and 1,3-dichloropropane. No further attempts at product identification were made.

Photolysis of an *N*-halo amide presumably yields both halogen atoms and amidyl radicals, and the former, particularly Cl·, presumably react (mainly) with the solvent to produce carbon-centered radicals. Since such radicals are not observed in these systems (i.e., the EPR spectra of the amidyls are all completely clean), their stationary-state concentration must be very low. This result is consistent with the fact that halogen atom abstraction by the cyclohexyl radical from *N*-chloro- and *N*-bromo-*N*-ethylpropionamide appears to be a fairly rapid process (vide infra).

The bimolecular rate constants for decay ($2k_t$) cover a wide range of values, and their magnitude is clearly determined by steric factors. Relatively unhindered radicals such as $CH_3CH_2\dot{N}C(O)C_2H_5$, $CH_3\dot{N}SO_2CH_3$, and $(CH_3)_2CH\dot{N}C(O)OC_2H_5$ decay at rates that must be close to the diffusion-controlled limit. Slightly more hindered radicals such as $CH_3\dot{N}C(O)C(CH_3)_3$, $(CH_3)_3CCH_2\dot{N}C(O)CH_3$, and $C_2H_5\dot{N}SO_2CH_3$ decay rather more slowly, while $(CH_3)_2CH\dot{N}SO_2CH_3$ and all the *N*-*tert*-butyl amidyl radicals decay at rates that are well below the diffusion-controlled limit. This is clearly due to an enthalpic barrier to reaction rather than to an entropic barrier; i.e., for $(CH_3)_2CH\dot{N}SO_2CH_3$, $(CH_3)_3C\dot{N}C(O)C(CH_3)_3$, $(CH_3)_3C\dot{N}C(O)OC_2H_5$, and $(CH_3)_3C\dot{N}SO_2CH_3$, the measured activation energies (E_t) are 3.1, 5.1, 4.1, and ca. 6.0 kcal/mol, respectively, and the preexponential factors are $10^{10.5}$, $10^{11.0}$, $10^{10.8}$ and ca. $10^{8.8}$ M^{-1} s^{-1}, respectively. In this respect, therefore, amidyl radicals show the same type of response to steric hindrance as do certain other nitrogen-centered radicals such as dialkylaminyl,[57,58] dialkylaminium,[59] and dialkylketiminyl[60,61] radicals. However, their response does differ from that observed with dialkyl nitroxides[62-64] and acyl alkyl nitroxides,[65] for which sterically induced retardation of the bimolecular self-reaction manifests itself in the entropy, rather than in the enthalpy, of reaction.

The reactivities of all *N*-*tert*-butyl amidyl radicals will no doubt be lower than those of less hindered amidyl radicals in a wide variety of intermolecular reactions, which could explain why intramolecular H-atom abstraction from a suitable acyl group is much more pronounced for *N*-*tert*-butyl than for *N*-methyl amidyl radicals.[52] It is also worth noting that since the $(CH_3)_3C\dot{N}C(O)C(CH_3)_3$ radical decayed with clean second-order kinetics even at 281 K, the potential first-order decay reactions

$$(CH_3)_3C\dot{N}C(O)C(CH_3)_3 \rightarrow (CH_3)_2C{=}NC(O)C(CH_3)_3 + CH_3\cdot$$

$$(CH_3)_3C\dot{N}C(O)C(CH_3)_3 \rightarrow (CH_3)_3CN{=}C{=}O + (CH_3)_3C\cdot$$

must have rate constants $<10^2$ s^{-1} at this temperature. A similar conclusion applies to the analogous potential first-order decay reactions of $(CH_3)_3C\dot{N}C(O)OC_2H_5$.

Although our attempts to study the decay of $CH_3\dot{N}C(O)CH_3$ were frustrated by the poor solubility of the parent *N*-chloro amide in cyclopropane, our results with the other amidyls leave no doubt that under our conditions this radical would decay with second-order kinetics at the diffusion-controlled limit. This contrasts with Tam et al.'s[10] finding that when generated by photolysis at low light intensities[13] of *N*-nitroso-*N*-methylacetamide in benzene at 298 K, this radical decayed with first-order kinetics, the measured rate constant for decay increasing with increasing concentration of the nitroso compound. Nitroso amides would therefore appear to be less satisfactory sources of amidyl radicals for kinetic studies than *N*-chloro or *N*-bromo amides.

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Hydrogen Atom Abstraction by the $C_2H_5\dot{N}C(O)C_2H_5$ Radical. The data summarized in Tables VI and VII show that the thermally initiated reaction of *N*-halo-*N*-ethylpropionamide with cyclohexane in benzene containing trichloroethylene is a free-radical chain reaction. After correction of the measured rates for the self-reaction of the halo amide, the kinetics for both chlorination and bromination obey eq III. The kinetics also meet the more stringent requirement that $\rho_{corr}/[C_6H_{12}](R_i)^{1/2}$ should have the same value (within experimental error) for chlorination and bromination. We therefore equate the mean value of this quantity from all experiments, viz., 0.083 $M^{-0.5}$ $s^{-0.5}$, with the ratio of the rate constant for hydrogen atom abstraction from cyclohexane by the $C_2H_5\dot{N}C(O)C_2H_5$ radical divided by the square root of the rate constant for the bimolecular self-reaction of this radical, i.e., $k_2/(2k_5)^{1/2}$. Since the bimolecular self-reaction of $C_2H_5\dot{N}C(O)C_2H_5$ radicals is diffusion controlled, we estimate that $2k_5$ (= $2k_t$) has a value of ca. 6.0×10^9 M^{-1} s^{-1} at 301 K, this estimate being based on the data tabulated by Lehni et al.[66] for the diffusion-controlled bimolecular self-reaction of benzyl radicals in a cyclohexane/toluene solvent mixture at this temperature. Combining this value for $2k_5$ with the mean value for $k_2/(2k_5)^{1/2}$ yields $k_2 \simeq 6.4 \times 10^3$ M^{-1} s^{-1} at 301 K.

Our value of k_2 is in reasonable agreement with Tam et al.'s[10] flash photolytic rate constant for hydrogen abstraction from cyclohexane by the $CH_3\dot{N}C(O)CH_3$ radical, viz., 1.85×10^4 M^{-1} s^{-1} at 298 K. The magnitude of these two rate constants shows that unhindered amidyl radicals are much more reactive in hydrogen abstraction than the highly hindered $(CH_3)_3C\dot{N}SO_2CH_3$ radical (vide supra). They are also more reactive than dialkylaminyl radicals[57] and dialkylaminium radicals.[59] A recent report[67] that the cyclic 3,3-dimethylglutarimidyl radical $\overline{O{=}CCH_2CMe_2CH_2C(=O)\dot{N}}$· abstracts hydrogen from cyclohexane with a rate constant of 3.5×10^3 M^{-1} s^{-1} at room temperature is rather surprising since one might have expected imidyl radicals to be more reactive than amidyl radicals.

The *N*-halo-*N*-ethylpropionamide/cyclohexane reactions appear to follow kinetic equation III over the entire range of reagent concentrations examined (see Tables VI and VII). The rate constants k_1 for both chlorine atom and bromine atom abstraction from their haloamides by the C_6H_{11}· radical can therefore be calculated[54] to be $\geq 2 \times 10^4$ M^{-1} s^{-1} at 301 K.

The self-reaction of $C_2H_5N(Cl)C(O)C_2H_5$ is faster than that of $C_2H_5N(Br)C(O)C_2H_5$ in the absence of C_2HCl_3 (see Table IV), but the reverse is true in the presence of this halogen atom trap (see Tables VI and VII). This implies that destruction of the chloroamide by a chlorine atom chain is considerably faster than the destruction of the bromo amide by a bromine atom chain but that the bromo amide is actually more reactive toward free radicals than the chloro amide.[68] We tentatively suggest that the C_2HCl_3-inhibited halo amide self-reaction is a chain process that can be represented by the following reactions:

$$C_2H_5\dot{N}C(O)C_2H_5 + C_2H_5N(X)C(O)C_2H_5 \rightarrow C_2H_5NHC(O)C_2H_5 + CH_3CH{=}NC(O)C_2H_5 + X\cdot$$

$$X\cdot + H(Cl)C{=}CCl_2 \rightarrow H(Cl)C(X)\dot{C}Cl_2$$

$$H(Cl)C(X)\dot{C}Cl_2 + C_2H_5N(X)C(O)C_2H_5 \rightarrow H(Cl)(X)CCl_2X + C_2H_5\dot{N}C(O)C_2H_5$$

Finally, we note that repeated attempts to study the kinetics of the free-radical halogenation of toluene by *N*-halo-*N*-ethylpropionamide were uniformly unsuccessful, apparently because the halogen atom chain could not be suppressed completely. Similar problems have been reported in several other attempted kinetic studies of alkylaromatic halogenation by organic halogenating reagents.[47,51,69,70] A few competitive experiments involving toluene/cyclohexane and $C_2H_5N(X)C(O)C_2H_5$ were also unsuccessful because of incomplete suppression of the chlorine atom chain and because the method used to analyze the bromination products (GC) led to decomposition of the bromoamide and its reaction with the substrates on the GC column.

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Registry No. $(CH_3)_3CCH_2\dot{N}C(O)OC_2H_5$, 82890-87-7; $(CH_3)_2CH\dot{N}C(O)OC_2H_5$, 82890-88-8; $(CH_3)_3C\dot{N}C(O)OC_2H_5$, 82890-89-9; $CH_3\dot{N}COC_2H_5$, 74260-27-8; $(CH_3)_3CCH_2\dot{N}COC_2H_5$, 76826-94-3; $CH_3\dot{N}C(O)CH(CH_3)_2$, 82890-90-2; $C_2H_5\dot{N}C(O)C_2H_5$, 74260-28-9; $(CH_3)_3CCH_2\dot{N}C(O)CH_3$, 76826-93-2; $(CH_3)_2CH\dot{N}C(O)CH_3$, 38479-74-2; $(CH_3)_2CH\dot{N}C(O)C_2H_5$, 74260-29-0; $(CH_3)_3C\dot{N}C(O)CH_3$, 38479-76-4; $(CH_3)_3C\dot{N}C(O)C_2H_5$, 76826-96-5; $(CH_3)_3C\dot{N}C(O)C(CH_3)_3$, 76826-97-6; $CH_3\dot{N}SO_2CH_3$, 74387-87-4; $C_2H_5\dot{N}SO_2CH_3$, 74387-88-5; $(CH_3)_2CH\dot{N}SO_2CH_3$, 74387-89-6; $(CH_3)_3C\dot{N}SO_2CH_3$, 66031-77-4; $(CH_3)_2CH\dot{N}C(O)OC_2H_5$, 82890-88-8; $(CH_3)_3C\dot{N}C(O)OC_2H_5$, 82890-89-9; $(CH_3)_3CN(Cl)SO_2CH_3$, 2547-65-1; $(CH_3)_3CN(Br)SO_2CH_3$, 66031-82-1; $C_2H_5N(Cl)C(O)C_2H_5$, 82890-91-3; $C_2H_5N(Br)C(O)C_2H_5$, 82890-92-4; C_6H_{12}, 110-82-7; H_2, 1333-74-0; C_2HCl_3, 79-01-6; TBHN, 14976-54-6.

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