

ADDITION OF PHENYL RADICAL TO t-BUTYL ISOCYANIDE

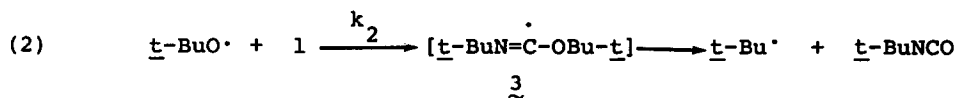
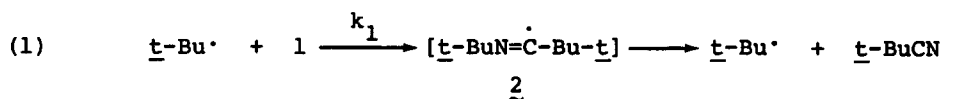
AN EXAMPLE OF A CYANIDE TRANSFER REACTION

Sung Soo Kim¹

Department of Chemistry
University of Southern California
Los Angeles, California 90007 U.S.A.

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Previously², we reported that both t-butyl and t-butoxy radicals efficiently add to t-butyl isocyanide (1). The former initiates a radical chain isomerization of 1 to pivalonitrile (Eq. 1) while the latter oxidizes 1 to t-butyl isocyanate (Eq. 2). These and other³ results point to imidoyl radicals 2 and 3 as intermediates.



In this paper we report our findings on the addition of phenyl radical to 1 at 100°C, yielding imidoyl radical 4 which cleaves to benzonitrile and t-butyl radical. Whereas it could be argued that the mechanism proposed in Eq. 1 is clouded by the possibility of the unimolecular isonitrile to nitrile rearrangement⁴, the present results clearly show the *intermolecularity* of this radical-induced reaction.

Reaction at 100°C of degassed and sealed Pyrex tubes containing variable molar concentrations of 1 and cumene (as competitive scavengers of phenyl radical) with 5 mM benzoyl peroxide (BP) in chlorobenzene led to the formation of pivalonitrile, benzene and benzonitrile as shown in Table 1.

Table 1: Products From the Reaction of Variable *t*-Butyl Isocyanide and Cumene With Benzoyl Peroxide (BP) (0.005 M) in Chlorobenzene for 7 Half-Lives of BP at 100°C.^a

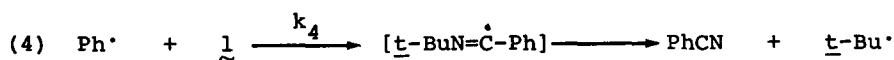
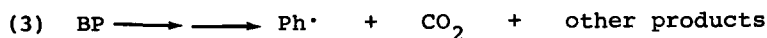
<u>REACTANTS</u>		<u>PRODUCTS</u>				
<u>t</u> -Butyl-Isocyanide	Cumene	Benzonitrile		Benzene	Pivalonitrile	
	<u>M</u>			<u>mM</u>		<u>mM</u>
a	b	a/b	c	d	c/d	
1.50	5.92	0.250	4.70	2.50	1.88	97.0
1.43	4.58	0.313	4.85	2.40	2.02	125.0
2.03	5.55	0.366	4.90	1.68	2.92	149.0
1.96	4.43	0.442	5.47	1.88	2.91	184.0
2.53	5.09	0.500	5.34	1.53	3.49	222.0

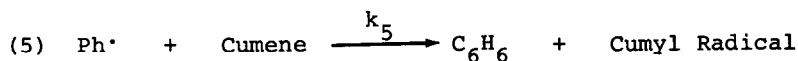
^a BP had decomposed over 99% after 3 1/2 hr. at 100°C.

^b Products analyses were carried out by vpc using 12 ft, 20% TCEP on chromsorb P P column at 50°C for benzene at 100°C for pivalonitrile and at 150°C for benzonitrile.

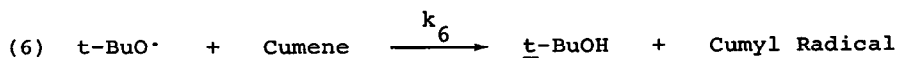
As previously noted², Eq. 1 is very efficient since it "turns over" 20-40 times for each BP decomposition leading to increasing yields of pivalonitrile with increasing $[I]/[cumene]$. The reaction scheme required to explain the products in Table 1 consists of Eq. 1 and Scheme 1 below.

Scheme 1





The formation of benzonitrile shows the intermolecular feature of the radical-induced isonitrile to nitrile conversion. The large ratios of [scavenger]/[BP] ≥ 300 leads to pseudo-first order kinetics so that from Eqs. 3, 4 and 5, $[\text{PhCN}]/[\text{C}_6\text{H}_6] = [k_4/k_5] ([\text{I}]/[\text{cumene}])$. The data in Table 1 provides $[k_4/k_5] = 7.1 \pm 0.5$. From our previous study with *t*-butoxy radical², $k_2/k_6 = 0.84 \pm 0.16$.



From literature sources⁵, we estimate $k_5 \approx 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ which leads to $k_4 \approx 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at 100°C. Previously², we estimated $k_2 \approx 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ at 125°C. For further comparison, from a gas phase study, the addition of methyl radical to methyl isocyanide shows $k = 6.15 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ at 105°C⁶. Assuming *t*-butyl and methyl isocyanide to be equivalent substrates in these radical additions, and assuming no significant difference between reactions carried out in the gas phase and hydrocarbon media, we conclude that the relative reactivity order of radical addition to isocyanides is phenyl \gg *t*-butoxy, methyl.

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References

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5. The rate constant for hydrogen atom abstraction by phenyl radical from toluene is $\sim 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ at 40° and the relative reactivity of toluene and cumene towards phenyl radical at 60° is 1:3.4 suggesting $k_5 \sim 10^7 \text{ M}^{-1} \text{ sec}^{-1}$. See K. U. Ingold in Free Radicals, Vol. 1, J. Kochi, ed., J. Wiley and Sons, Inc., New York, N. Y., 1973, p 73.
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