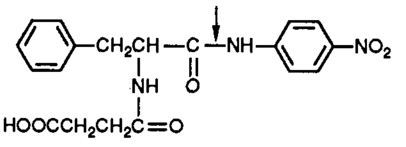
Table I. Normalized Rates of Hydrolysis of **2** by α-Chymotrypsin Immobilized in the Photochromic Copolymer at Different Degrees of Loading[a]

	load (mol %) =				
	0.18	0.3	0.5	0.75	1
v_{cis}	5	4	4	1	1
v_{trans}	2	1	0–0.3	1	1

[a] A value of 1 corresponds to a rate of 0.5 μM min^{-1} of *p*-nitroaniline formation.

In fact, a photostationary cis/trans equilibrium corresponding to 1.04 is obtained. Illumination of the resulting *cis*-azobenzene polymer, λ > 400 nm, restores almost entirely the *trans*-azobenzene polymer.

Photoregulation of α-chymotrypsin is studied by cutting slices of the photochromic polymer, ca. 2 mm wide, that include 47.6 units of immobilized enzyme and following the rate of hydrolysis of *N*-(3-carboxypropionyl)-L-phenylalanine *p*-nitroanilide[16] (**2**), 5.7 × 10^{-3} M, by the immobilized enzyme. Figure 1 shows the cyclic photoregulation of the biocatalyst immobilized in a polymer that includes 0.5 mol % of the photochromic component in the copolymer structure: No hydrolysis of **2** occurs by the enzyme entrapped in the *trans*-azobenzene copolymer, Figure 1a. Photoisomerization of the copolymer to *cis*-azobenzene results in a biocatalytic assembly that effectively hydrolyzes the substrate at a rate of 2 μM min^{-1}, Figure 1b. Further illumination of the polymer–enzyme assembly, λ > 400 nm, restores the *trans*-azobenzene polymer, and the enzyme is again deactivated, Figure 1c. Additional illumination, λ = 330–370 nm, of the copolymer and production of the *cis*-azobenzene polymer restores the biocatalytic activity of the assembly, Figure 1d. It is evident that the biocatalytic transformation is completely and reversibly "on-off" switchable in the photochromic copolymer–enzyme assembly. Control experiments reveal that the activity of α-chymotrypsin in the *cis*-azobenzene copolymer is ca. 2-fold faster than the activity of the enzyme in a pure acrylamide gel. The switching efficiency of immobilized α-chymotrypsin and its activity strongly depend on the loading degree of the polymer by the photochromic material, Table I. It is evident that, at low loading degrees of the copolymer by the photochromic material, incomplete switching of the biocatalytic assembly is obtained, and as the loading degree increases up to a value of 0.5%, the activity of the enzyme in the *trans*-azobenzene copolymer structure declines. At 0.5% loading, complete switchable activity of the biocatalyst is observed. Further increase of the loading decreases the biocatalyst performance in both photochromic forms of the polymer.



2

The photostimulated activity of the enzyme in the functionalized polymer could originate from structural changes of the protein backbone induced by the volume changes of the polymer. Alternatively, photoregulation of the permeabilities of the polymer backbone[17] toward the substrate (**2**) might photoregulate the entrapped biocatalyst.

Gel filtration and flow dialysis experiments reveal that *trans*- and *cis*-**1**-acrylamide copolymers differ substantially in their permeabilities toward the substrate **2**. We find that *cis*-**1**–acrylamide is permeable toward the substrate, while *trans*-**1**–acrylamide is essentially nonpermeable toward it. We thus conclude that photoregulation of α-chymotrypsin immobilized in the photochromic azobenzene copolymer is controlled by the permeability of the substrate across the polymer matrix. Application of other photochromic polymers and immobilization of different enzymes are being further examined as photoregulated biocatalytic assemblies.

Acknowledgment. The support of Niedersachsen Land Foundation, FRG, is gratefully acknowledged.

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[17] Aoyama, M.; Watanabe, J.; Inoue, S. *J. Am. Chem. Soc.* **1990**, *112*, 5542.

Partial Oxidation of Olefins by Molecular Oxygen Catalyzed by (Alumina)Rh(O_2)

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Direct, partial oxidation of an olefinic double bond by molecular oxygen, catalyzed by a metal complex, is rare,[1] but we have now found a novel example: oxide-bound species (alumina)Rh(O_2)[2] efficiently catalyzes reaction between O_2 and olefins to give ketones. In this procedure, no "sacrificial" ligands are required,[3] and under our conditions, little combustion or double-bond cleavage[4] is noted. Thus, this new reaction is fundamentally different from those based on soluble Rh(O_2) complexes,[3,4] including organic oxygen-ligated (acac)Rh(O_2),[4] and product distributions and relative olefin reactivities show it to be unlike Wacker[1c] or radical[5] oxidation pathways.

The catalyst (alumina)Rh(O_2) was prepared[2,6] by reaction between Rh(allyl)$_3$ and alumina followed by carbonylation[7] and O_2 treatment.[2] When a stream of O_2 (ca. 1 atm) was passed through a reservoir of cyclohexene and then over a frit charged with 100 mg of (alumina)RhO_2 (5.6 μmol of Rh) at 280 °C for 4 h, cyclohexanone (6.0 mg; 61 μmol; 2.7 equiv (equiv of Rh)$^{-1}$ h^{-1}) was collected in a cold trap (−78 °C); no products of allylic attack were obtained, suggesting that radical pathways are not important with this system.[5] Similarly, when a stream of O_2 was passed first through norbornene[8] and then over the catalyst, GC analysis showed that 2-norbornanone (416 mg; 3.8 mmol; 168 equiv (equiv of Rh)$^{-1}$ h^{-1}) and cyclohexene-4-carboxaldehyde (178 mg; 1.6 mmol; 72 equiv (equiv of Rh)$^{-1}$ h^{-1}) were produced,[9] and 2,3-dimethyl-2-butene gave pinacolone (437 mg; 4.4 mmol; 260 equiv (equiv of Rh)$^{-1}$ h^{-1}).[10] These observed skeletal rear-

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[1] (a) The outstanding example of an O_2-based process is silver-catalyzed ethylene oxidation to ethylene oxide. See, for example: Lee, J. K.; Verykios, X. E.; Pitchai, R. *Appl. Catal.* **1989**, *50*, 171. Sarjkowski, D. J.; Boudart, M. *Catal. Rev. Sci. Eng.* **1987**, *29*, 325. (b) For another example of direct O_2 involvement, see: Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790. Marchon, J.-C.; Ramasseul, R. *J. Chem. Soc., Chem. Commun.* **1988**, 298. (c) Our process stands in contrast to "Wacker" oxidation in which oxygen acts as an *indirect* oxidizing agent which reoxidizes the used catalyst. See: Henry, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 1595.

[2] Fischer, H. E.; Schwartz, J. *J. Am. Chem. Soc.* **1989**, *111*, 7644.

[3] (a) Dudley, C. W.; Read, G.; Walker, P. J. C. *J. Chem. Soc., Dalton Trans.* **1974**, 1926. (b) Ingersheim, F.; Mimoun, H. *Nouv. J. Chim.* **1980**, *4*, 161.

[4] Bönnemann, H.; Nunez, W.; Rohe, D. M. M. *Helv. Chim. Acta* **1983**, *66*, 177.

[5] For example, see: Lyons, J. E.; Turner, J. O. *J. Org. Chem.* **1972**, *37*, 2881.

[6] For example, 30 mg of Rh(allyl)$_3$ was treated with a slurry of 1 g of Degussa aluminum oxide C (100 m^2 g^{-1}; dried at 250 °C) in toluene at room temperature for 96 h. After removal of the toluene, 1 atm of CO was passed over the resulting powder at room temperature for 12 h,[7] followed by treatment with dry O_2 (1 atm) at 140 °C for 170 h.[2] The resulting catalyst was 1.1% Rh by weight.

[7] McNulty, G. S.; Cannon, K.; Schwartz, J. *Inorg Chem.* **1986**, *25*, 2919.

[8] A warmed reservoir was used to maintain the olefin in liquid form.

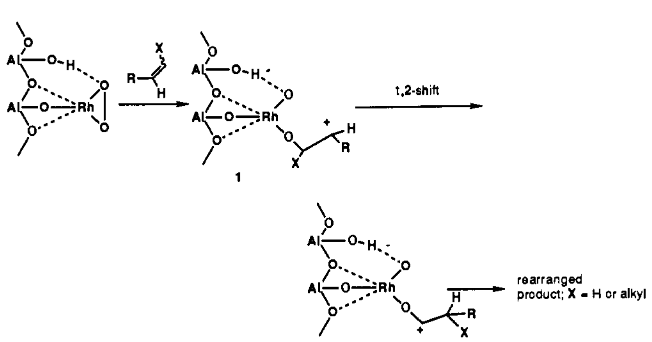
[9] No oxidation was observed catalyzed by the support in the absence of the Rh complex.

Table I. Olefin Oxidation by O_2 Catalyzed by (Alumina)Rh(O_2)

olefin	products[a]	mol[b] mol_{Rh}^{-1} h^{-1}	rel rate
propene	acetone	70	26
propene[c]	acetone (94); propanal (6)	60	22
2,3-dimethyl-2-butene	pinacolone (93); acetone (7)	280	104
2-norbornene	2-norbornanone (70); cyclohexene-4-carboxaldehyde (30)	240	89
p-methoxystyrene	*p*-methoxyacetophenone (>95); (*p*-methoxyphenyl)acetaldehyde (<5)	240	89
p-methylstyrene	*p*-methylacetophenone (79); *p*-tolylacetaldehyde (21)	160	59
styrene	acetophenone (80); phenylacetaldehyde (20)	120	44
p-chlorostyrene	*p*-chloroacetophenone (>90); (*p*-chlorophenyl)acetaldehyde (<10)	110	41
p-nitrostyrene	*p*-nitroacetophenone (>90); (*p*-nitrophenyl)acetaldehyde (<10)	43	16
cyclohexene	cyclohexanone	2.7	1

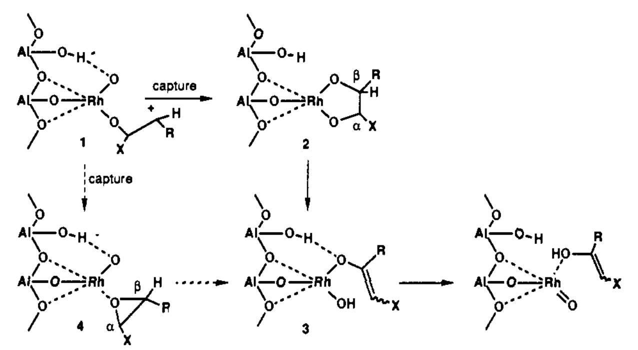
[a] Relative percent where indicated in parentheses. [b] Total product yield. [c] Water vapor present in propene stream.

Scheme I. Olefin Oxidation by O_2 Catalyzed by (Alumina)Rh(O_2) Involves a Cationic Intermediate



rangements indicate an oxidation pathway involving a cationic intermediate. Interestingly, when propene was oxidized in this manner, acetone (295 mg; 5.1 mmol; 70 equiv (equiv of Rh)$^{-1}$ h^{-1}), not propanal, the expected product of a cationic intermediate, was the major product; however, when the reagent gas stream was also passed through water, some propanal was produced (15 mg; 1.3 mmol; 2 equiv (equiv of Rh)$^{-1}$ h^{-1}). Consistent with a cationic mechanism, oxidation of 2,3-dimethyl-2-butene was much faster than that of propene, and rates for oxidation of a series of styrenes correlated in the order of substituent group donor abilities (σ_p^+; p-NO$_2$ < p-Cl < p-H < p-CH$_3$ < p-OCH$_3$; 0.36:0.92:1:1.3:2; figure available as supplementary material).[11] For the styrenes,[8] as with propene, ketones were the major products (Table I).[12] In control experiments, it was shown that propylene glycol gives acetone over the alumina-bound catalyst under the oxidation reaction conditions. Similarly, (1,2-dihydroxyethyl)benzene (from styrene) reacts over the catalyst to give, extensively, acetophenone. Thus glycols or glycolates are viable candidates as precursors of the observed ketones.

Scheme II. Cationic Species Collapse to the Ketone Precursor Might Involve an Enolate



While details of catalyst reactivity remain to be elucidated, the fundamental aspect of olefin oxidation by the Rh complex is already clear: olefin oxidation occurs through a cationic route. We propose (Scheme I) that the olefin attacks the dioxygen ligand (which may be activated by hydrogen bonding to a surface OH-group proton[13]) to give intermediate **1**, which can rearrange by a 1,2 hydride or alkyl shift. Control experiments show that glycols can give ketones over the catalyst; therefore we suggest that **1** can also be trapped to give glycolate **2** (Scheme II). β-Proton transfer to Rh–O in the glycolate,[14] **2**, would give ketone enolate **3**, and proton transfer in **3** would give the ketone (via the enol).[15-18] In the presence of water, protonation at oxygen might make collapse

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(10) For comparison purposes, a standard inorganic impregnation method was examined for catalyst preparation. $RhCl_3 \cdot 3H_2O$ (250 mg) was added to a slurry of 2 g Degussa aluminum oxide C in 50 mL of water. The mixture was stirred for 24 h and was then filtered. The solid was dried at 150 °C for 2 h and was then pulverized to give a pink powder. Carbon monoxide (1 atm) was passed at 100 °C over this powder for 24 h. The color changed to yellow, and IR analysis[7] showed broad bands at 2012 and 2095 cm^{-1}. Ozonolysis (1% O_3 in O_2) of this yellow material at room temperature for 4 h resulted in the disappearance of the IR adsorption and a color change to off-white. The Rh content of this material was 3% by weight. When O_2 and norbornene were treated with this material under standard conditions, norbornanone (relative yield 70%) and cyclohexene-4-carboxaldehyde (relative yield 30%) were produced (total, 160 equiv (equiv of Rh)$^{-1}$ h^{-1}). In the absence of the intervening carbonylation step, no decolorization was noted on ozonation, and no oxidation catalysis was observed.

(11) Rates for "Wacker" oxidation of olefins correlate *inversely* with attachment of donor substituents. In fact, a recent patent for a "heterogeneous" Wacker-like oxidation based on Re oxides supported on alumina reports that, unlike our system in which they are highly reactive, branched olefins are unreactive with that catalyst (Yeh, C. Y.; Savini, C. U.S. Patent 4,560,803, 1985). For epoxidations by peracids, for which rates correlate *directly* with attachment of donor substituents, see: Lynch, B. M.; Pausacher, K. M. *J. Chem. Soc.* **1955**, 1525. The possibility that radical cationic intermediates, formed by electron transfer from the olefin to the catalyst, are initially involved cannot be rigorously excluded. See: Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1988**, *110*, 1953.

(12) Under typical conditions, 3–5 g of olefin was passed over the catalyst and conversions of 3–7% were realized. No attempts have yet been made to optimize conversions or rates. Mass balance for norbornene was confirmed as follows. Norbornene (16.9 g) was passed over 100 mg (8.5 μmol of Rh) of the catalyst at 280 °C in a stream of O_2 as described in the text. Effluent was collected in a weighed receiver and was analyzed by GC. In this way, it was demonstrated that >95% of the charged amount of norbornene was recovered as either unreacted olefin or norbornanone and cyclohexene-4-carboxaldehyde. Prior to and following this run, the catalyst was analyzed for Rh content (before use, 0.88%; following use, 0.86%). Used catalyst was reconverted to (alumina)Rh(CO)$_2$ under standard carbonylation conditions[7] as described above. Carbonylated catalyst was indistinguishable by IR from authentic (alumina)Rh(CO)$_2$.

(13) For protonic activation of a (dioxygen) ligand, see: White, R. E.; Coon, M. J. *Annu. Rev. Biochem.* **1980**, *49*, 315. The thermal stability of the (dioxygen) ligand has not yet been determined under the reaction conditions. Were the (dioxygen) complex to rearrange to a *cis*-dioxo analogue, attack on an oxo ligand would also give **1**.

(14) Over alumina, propylene glycol undergoes the expected (cationic intermediate) dehydration to propionaldehyde, and (1,2-dihydroxyethyl)benzene gives phenylacetaldehyde (for examples of vapor-phase dehydration of glycols over alumina by cationic intermediate pathways, see: Dana, G.; Wiemann, J. *Bull. Soc. Chim. Fr.* **1970**, 3994). That dehydration by the support and the catalyst give different product distributions suggests that different mechanisms are involved.

(15) Epoxides also rearrange rapidly over alumina to give products of cationic intermediates (see, for example: Rickborn, B.; Gerkin, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 1693). Thus, *free* epoxides or *free* glycols could be the precursor of the phenylacetaldehydes or propanal observed in these oxidation reactions. *Coordinated* epoxides (**4**) cannot be ruled out as precursors of the observed ketones, but reactivity of the free epoxide over the support is too great to enable definitive conclusions by way of simple control experiments: a rhodium metallaoxetane[16] has been postulated as in intermediate in the catalyzed rearrangement of an epoxide to a ketone via an enolate.[16d]

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(17) The small amount of C=C cleavage found for propene could also derive from the glycolate. See: Bönnemann, H.; Brijoux, W.; Pingel, N.; Rohe, D. M. M. *Catalysis of Organic Reactions*; Augustine, R. L., Ed.; Marcel Dekker: New York, 1985; p 309.

(18) The recently described oxidation of styrene in UHV by Rh(111)-p-(2×2)-O to acetophenone has not yet been mechanistically elucidated. See: Xu, X.; Friend, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 4571.

of oxyrhodium species **1** to the glycolate less kinetically favorable, enabling 1,2-shift pathways to compete.[19]

The simplicity of the oxidation system described above in terms of catalyst synthesis, resiliency of its ligand environment, and simple oxidation reagent requirement suggests its practicality for partial oxidation of olefins. Optimization studies, as well as those of catalyst recycle and other catalyst analogues, are now under way.

Acknowledgment. We acknowledge support for this work given by the National Science Foundation and the Sun Foundation.

Supplementary Material Available: A plot of relative rate data for oxidation of several styrenes (1 page). Ordering information is given on any current masthead page.

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(19) Interestingly, for propene oxidation, addition of water enhances the relative yield of non-"Wacker" product, propanal.

Surface Chemistry on Colloidal Metals: A High-Resolution Nuclear Magnetic Resonance Study of Carbon Monoxide Adsorbed on Metallic Palladium Crystallites in Colloidal Suspension

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There is a continuing interest in the spectroscopic characterization of small molecules adsorbed on the surfaces of catalytically interesting metal particles. Several fruitful studies have involved solid-state techniques such as solid-state and magic angle spinning NMR and surface vibrational spectroscopies, applied to supported metal particles. We have adopted an alternative approach to such surface species in an investigation of small molecules adsorbed on *colloidal* transition metals in the liquid phase, using spectroscopic techniques more often applied to molecular species in solution.

We have reported elsewhere the use of high-resolution liquid NMR to characterize carbon monoxide on highly dispersed colloidal palladium and platinum.[1] Those studies revealed ^{13}C chemical shifts near 200 ppm for adsorbed CO, and the absence of a Knight shift for the adsorbed CO, in contrast to the observations for CO on supported metallic crystallites of palladium,[2] was ascribed to pseudomolecular (nonmetallic) character in the colloidal metal particles, which were less than 20 Å in diameter. In this paper we describe the observation, by the same technique, of the adsorbed state of carbon monoxide on a palladium colloid of 70-Å mean diameter, a size range in which *metallic* character should manifest itself.

The palladium colloid was prepared by the reduction of palladium acetate to palladium metal by methanol in the presence of poly(vinylpyrrolidone) (PVP). Palladium acetate (50 mg) was added to a solution of PVP (MW 40 000; 2.5 g) in methanol (150 mL) and the mixture refluxed for 2 h. The resulting brown liquid was filtered (0.2-μm Teflon millipore) and concentrated to 25 mL. This procedure reproducibly yields colloidal palladium particles in the form of well-formed microcrystallites with a mean diameter (by transmission electron microscopy (TEM) and small angle X-ray scattering SAXS) of 70 Å. The colloid shows no tendency to precipitate on standing for at least several weeks. X-ray diffraction shows the presence of fcc palladium, with line widths consistent with the particle size shown by TEM and SAXS. Carbon monoxide adsorbs readily on the colloid in methanol, occupying only bridging sites (ν_{CO} 1944 cm^{-1}), similarly to CO on Pd(111) surfaces,[3] and consistent with the crystalline nature of the colloid particles. (On the smaller pseudomolecular Pd colloid, both bridging and terminal CO are observed.[1])

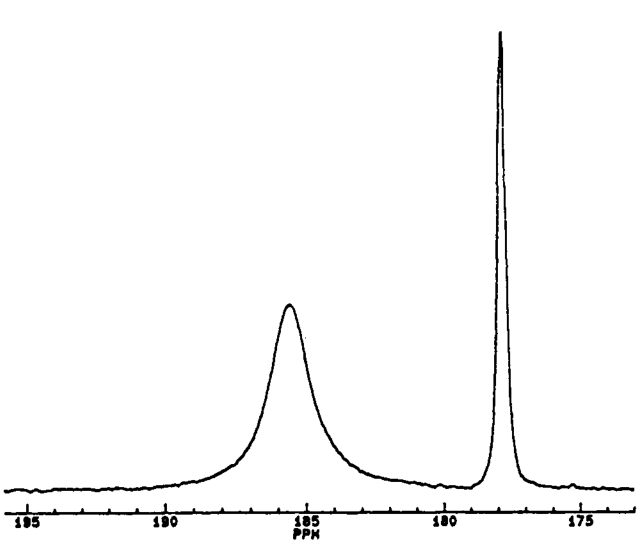

Figure 1. The carbonyl region of the room temperature ^{13}C NMR spectrum of the PVP stabilized Pd colloid under 3 atm of ^{13}CO. The spectrum is the result of 50 acquisitions taken with a 2-s recycle delay. Dissolved CO appears at 185.5 ppm and the PVP carbonyl at 178 ppm.

The carbonyl region of the 75-MHz room temperature ^{13}C NMR spectrum of a concentrated solution of the colloid under 3 atm of 99% ^{13}CO is shown in Figure 1. It consists of a resonance at 178 ppm due to the carbonyl group in PVP and a resonance at 185.5 ppm with a line width of 3 ppm. In variable-temperature studies the latter resonance reversibly narrows down to 233 K and broadens reversibly up to 348 K. The chemical shift is coincident with that observed for CO dissolved in a methanol solution of PVP (a resonance that shows no such variable-temperature behavior) and is thus assigned to dissolved CO, its width at 298 K being caused by chemical change, presumably with CO bound to the colloidal metal (vide infra). So far we have not been able to detect this species directly, which is hardly surprising, given its low concentration and probable line width. Solid-state ^{13}C NMR experiments performed at 198 K for CO adsorbed on Pd/η-alumina[2] (ca. 65 Å average diameter) show a broad, strongly Knight shifted peak[4] centered at 540 ppm with a half-width of 400 ppm (at room temperature this peak moves to 675 ppm and is narrowed to ca. 50 ppm by diffusion processes). Similarly, the room temperature ^{13}C chemical shift of CO adsorbed on Pd/SiO_2[5] is 750 ppm.

We have, however, observed the adsorbed CO resonance indirectly, using a variation of the Forsên–Hoffman spin saturation transfer experiment,[6] in which we measure the integrated intensity of the free CO resonance as a function of the frequency of a low-power, long-duration rf pulse, varied in increments of 25 ppm between +1400 and +200 ppm (see Figure 2). In addition, to establish a base line, for each such frequency, we also irradiated at its "mirror image" frequency, i.e., at the frequency displaced symmetrically with respect to the dissolved CO resonance (e.g., 170.5, 145.5, ..., −1214.5 ppm). A maximum (80%) saturation of the free CO resonance was observed at an irradiation frequency

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